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Silatropic Carbonyl Ene Cyclizations in the Synthesis of Pseudosugars and Hydroxylated Piperidines

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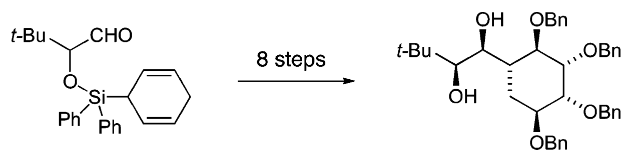
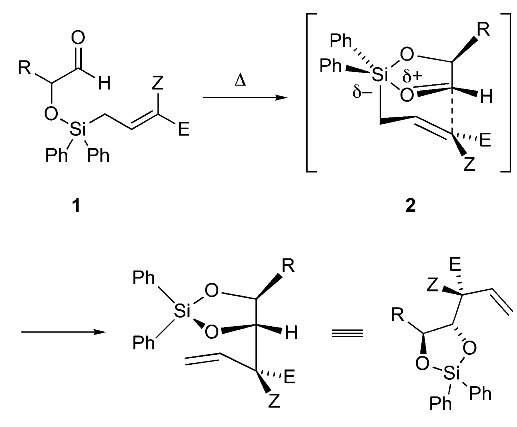


We describe two applications of silicon-tethered thermal allyl transfer reactions of α-silyloxyaldehydes; formally, these processes can be regarded as silatropic carbonyl ene reactions in which the silicon tether is transferred to the aldehyde oxygen concurrent with carbonyl allylation. In the first application, isoserinal substrates, which bear side-chain nitrogen functionality, are elaborated to dihydroxypiperidines. In the second application, a product of cyclohexadienyl transfer is taken on to carbocylic analogues of, for example, mannose. In both series, the silatropic ene reactions are effected thermally, with no added Lewis acid, and are both stereospecific and highly stereoselective.

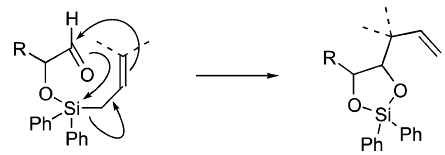
Introduction

Arising out of an ongoing investigation of the scope of silicon-tethered ene cyclizations, we discovered that substrates of the form **1** (Scheme 1) are converted into dioxasilolanes **3** upon heating.[1] We proposed that these reactions—which showed moderate to excellent stereoselectivity and very high stereospecificity—could proceed, in principle, by cooperative carbonyl and silyl activation by precomplexation (e.g., via **2**). Formally, the allyl transfer event is an unusual variant of the intramolecular ene reaction (Scheme 2), in which a silyl group is transferred rather than a proton; that is, a silatropic carbonyl ene reaction.[2] We have described generic reactions in both the α- and β-silyloxyaldehyde series;[1a,3] in this paper we extend the process to include substrates bearing side-chain amine functionality (leading to hydroxylated piperidines) and those bearing a more complex transferring allylic group (leading to pseudosugars).

SCHEME 1. Thermal Allylic Transfer Reactions via Aldehyde/Silyl Group Precomplexation



SCHEME 2. Formal Silatropic Carbonyl Ene Cyclization



Hydroxylated Piperidines. The therapeutic potential of hydroxylated piperidines, including iminosugars, derives in large part from the glycosidase inhibitory properties of the protonated form which is envisaged to mimic the transition state for acidic glycoside hydrolysis.

(1) (a) Robertson, J.; Hall, M. J.; Green, S. P. *Org. Biomol. Chem.* **2003**, *1*, 3635−3638. See also: (b) Bashiardes, G.; Chaussebourg, V.; Laverdan, G.; Pornet, J. *Chem. Commun.* **2004**, 122−123.

(2) For early studies on silatropic processes see: (a) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678−8685. (b) Coates, R. M.; Sandefur, L. O.; Smillie, R. D. *J. Am. Chem. Soc.* **1975**, *97*, 1619−1621. For a recent theoretical treatment supporting the concerted silatropic ene mechanism in the uncatalysed Mukaiyama aldol reaction see: (c) Wong, C. T.; Wong, M. W. *J. Org. Chem.* **2005**, *70*, 124−131. See also: (d) Dubac, J.; Laporterie, A. *Chem. Rev.* **1987**, *87*, 319−334.

(3) Hall, M. J. D.Phil. Thesis, University of Oxford, Oxford, U.K., 2003.

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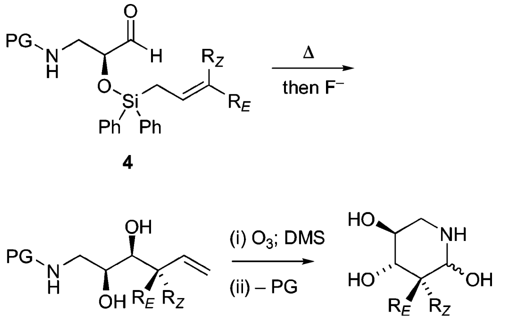
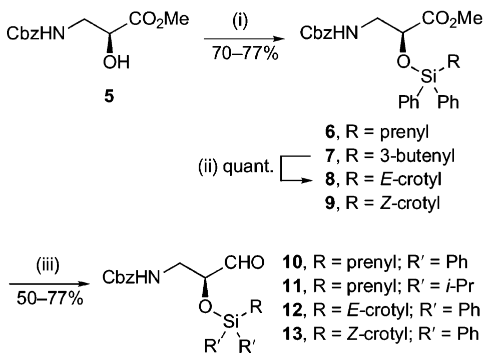
SCHEME 3. Application to Hydroxylated Piperidine Synthesis



SCHEME 4[a]



[a] Reagents: (i) $Ph_2Si(R)H$, $B(C_6F_5)_3$, CH_2Cl_2; (ii) $[(COD)Ir(PPh_2Me)_2]^+PF_6^-$ cat., CH_2Cl_2; (iii) DIBAL, CH_2Cl_2.

Numerous natural and nonnatural polyhydroxypiperidines have been screened in this capacity, and applications, in various stages of clinical and preclinical development, range from the treatment of diabetes, Gaucher's disease, and viral infections including influenza, hepatitis, and HIV. The area has been thoroughly reviewed.[4] Of note is that less highly oxygenated piperidines (di- and trihydroxylated) can also exhibit activity.[5]

Within this context, we envisaged application of our methodology to the synthesis of hydroxylated piperidines by incorporating amine functionality in the R-side-chain and effecting cyclization onto the internal carbon of the alkene formed during the silatropic ene reaction (Scheme 3).

This proposal required access to *O*-[(alk-2-enyl)diphenylsilyl]isoserinal derivatives (**4**); we had already prepared the *Si*-prenyl/*N*-Cbz derivative **10** (Scheme 4) for separate silicon-tethered Type I carbonyl ene cyclizations,[6] and for completeness, (*E*)- and (*Z*)-crotyl analogues **12** and **13**, respectively, were prepared using our earlier methodology.[7] On heating, prenyl substrate **10** cyclized smoothly, albeit slowly, generating the *trans*-substituted dioxasilolane **14** (Scheme 5) whose stereochemistry was established by NOE experiments (Table 1); this compound could not be purified by chromatography and was taken on crude into the desilylation which afforded *syn*-diol **16** in excellent overall yield. Interestingly, di(isopropyl)silyl substrate **11** cyclized under similar conditions; this time the dioxasilolane (**15**) was stable to chromatography and could be fully characterized. The fact that the reaction takes place with isopropyl- in place of phenyl-silyl substituents has implications for the mechanism of the formal silatropic ene process: the isopropyl substituents cannot be argued to facilitate a cooperative activation mechanism of the form implied in Scheme 1; they merely provide a steric impediment toward O−Si bond formation, and on the basis of this and other observations, we favor a mechanism closer to that implied by Scheme 2 in which the importance of carbonyl/silyl precomplexation is down-played. (*E*)-Crotyl substrate **12** cyclized to give apparently only one dioxasilolane (**17**) which was desilylated to *syn*,*syn*-diol **18**; in comparison, the cyclization of the (*Z*)-analogue (**13**) produced an 11:1 mixture of *syn*,*anti*-(**20**) and *anti*,*anti*-(**21**) diastereomers.

In all cases, the relative stereochemistry of the diols was confirmed by Corey−Winter elimination as summarized in Scheme 6. Corroboration of the stereochemistry at the methyl-bearing carbon was not sought, assignment being made by analogy to other cases in which the stereochemistry had been established by a bis(allylation)/RCM protocol;[1a] however, the specific rotations of compounds **23** {$[\alpha]^{22}_D$ −6.58° (*c* 0.73, $CHCl_3$)} and **24** {$[\alpha]^{22}_D$ +6.22° (*c* 0.37, $CHCl_3$)} supported the assignment that diastereomers **18** and **20** differed solely at the allylic methine center.

As an illustration of the synthetic potential of the silatropic ene products, the alkene in diol **16** was subjected to ozonolysis and the polar lactol **26** taken on directly into the hydrogenolysis step, *N*-deprotection being accompanied by amino-acetal reduction. Acetylation of this material (**27**), to aid purification (→ **28**), and subsequent partial deacylation led to the cyclic dihydroxypiperidine **29** in 18% yield over the four steps. This low yield was attributable largely to the ozonolysis reaction [step (i) → **26**, Scheme 7] that appeared to generate a number of polar, inseparable byproducts.

A significant improvement in overall yield was obtained simply by altering the order of events to aid purification at each stage. Diol acetylation (→ **30**) as the first step enabled a much cleaner ozonolysis to give an "anomeric" mixture (**31** and **32**) that was deprotected and reduced as before giving, after methanolysis, free dihydroxypiperidine **27**. The relative stereochemistry in this compound was confirmed by the magnitude of the $^3J_{3,4}$ coupling constant (9.4 Hz) indicative of diequatorial diol functionality.

Cyclohexadienyl Transfer. The potential of thermal silatropic ene reactions to offer stereoselective routes to useful synthetic intermediates and biologically active molecules would be limited if restricted merely to the formal transfer of simple allylic groups (allyl, prenyl, crotyl), and in more recent work we have focused on extending the methodology to the transfer of more complex groups (bearing, for example, γ-alkoxy or trialkylsilyl substitution).[8] Projecting a route into carbocyclic analogues[9] of higher sugars, our interest focused on

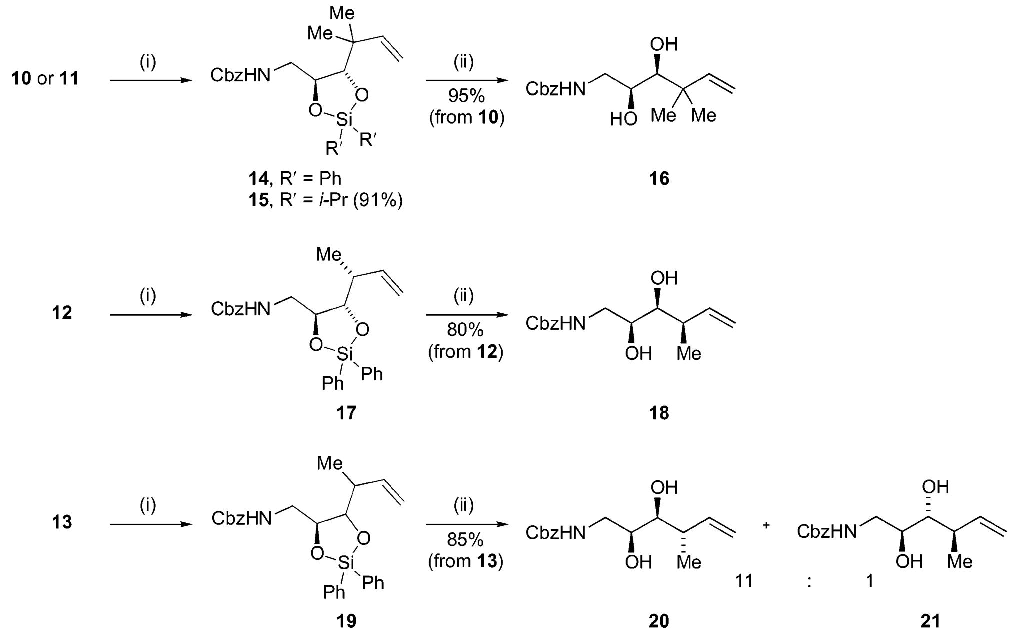
(4) Lillelund, V.; Jensen, H. H.; Liang, X. F.; Bols, M. *Chem. Rev.* **2002**, *102*, 515−553 and references therein.

(5) (a) Bernotas, R. C.; Papandreou, G.; Urbach, J.; Ganem, B. *Tetrahedron Lett.* **1990**, *31*, 3393−3396. (b) Ichikawa, Y.; Igarashi, Y.; Ichikawa, M.; Suhara, Y. *J. Am. Chem. Soc.* **1998**, *120*, 3007−3018. (c) Patil, N. T.; John, S.; Sabharwal, S. G.; Dhavale, D. D. *Bioorg. Med. Chem.* **2002**, *10*, 2155−2160.

(6) Robertson, J.; Hall, M. J.; Stafford, P. M.; Green, S. P. *Org. Biomol. Chem.* **2003**, *1*, 3758−3767.

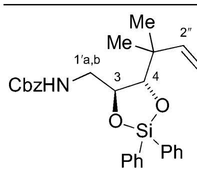
(7) (a) For the silylation procedure see: (a) Blackwell, J. M.; Foster, K. L.; Beck, V. H.; Piers, W. E. *J. Org. Chem.* **1999**, *64*, 4887−4892. The alkene isomerisation process was adapted from: (b) Matsuda, I.; Kato, T.; Sato, S.; Izumi, Y. *Tetrahedron Lett.* **1986**, *27*, 5747−5750.

SCHEME 5[a]



[a] Reagents: (i) $PhCH_3$, 120−130 °C, 17−24 h; (ii) KF, H_2O_2, aq. MeOH.

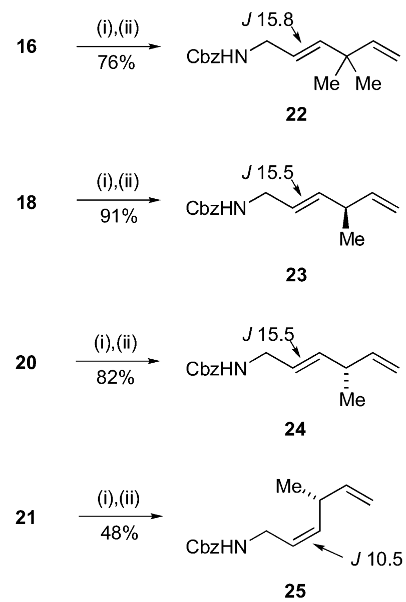
TABLE 1. NOE Results for Dioxasilolane 14

		enhancement/%				
	irradiate	H1′a	H1′b	3	4	2″
	H1′a		23.4	5.5	2.4	0.9
	H1′b	23.0		2.8	5.7	0.0
	3	3.0	1.5		1.7	2.4
	4	3.5	5.1	1.8		6.7
14	2″	0.0	0.0	3.6	3.8	

the possibility of tethered cyclohexadienyl transfer, in which cyclization via one of the diastereotopic olefins (**A** or **B**) would be expected to be preferred, leading to stereochemical control at the starred carbon (Scheme 8). The stereochemical situation is analogous to the preferred mode of cyclization (chairlike vs boatlike) for the (*Z*)-crotyl substrates, and cyclization through olefin **A** was predicted to lead to the *syn*,*anti*-configured product after desilylation (see below). Although such tethered variants are not precedented, the desymmetrization of silylated cyclohexadienes has been described for the synthesis of cyclitols and related compounds,[10] (±)-peduncularine,[11] and taxol intermediates.[12] Of particular relevance is Studer's recent development of stereoselective intermolecular carbonyl cyclohexadienylations using the corresponding silicon and titanium derivatives.[13]

To test this hypothesis, novel dialkyl(cyclohexadienyl)silanes **34** and **35** (Scheme 9) were prepared in excellent yield using variants of literature procedures.[10g,11] These

SCHEME 6[a]



[a] Reagents: (i) $(Im)_2C{=}S$, THF; (ii) $P(OEt)_3$.

(8) Robertson, J.; Tyrrell, A. T. Unpublished results, 2004. See also ref 3.

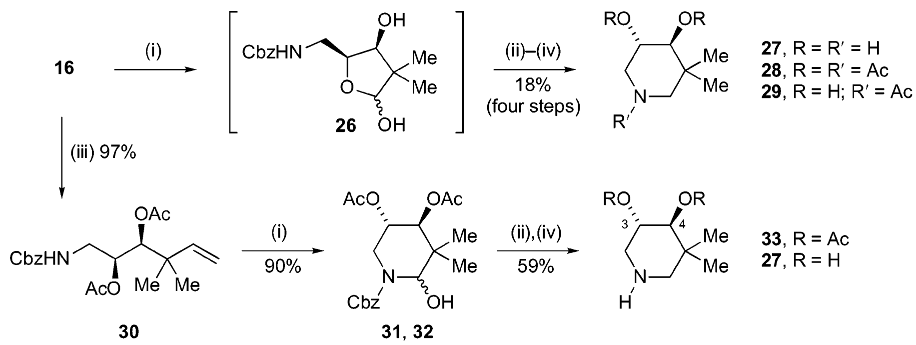
(9) (a) Rassu, G.; Auzzas, L.; Pinna, L.; Battistini, L.; Curti, C. Advances in Chemical Synthesis of Carbasugars and Analogues. In *Studies in Natural Products Chemistry*, Vol. 29, Part J; Atta-ur-Rahman, Ed.; Elsevier: Amsterdam, **2003**, 449−520. (b) Suami, T.; Ogawa, S. *Adv. Carbohydr. Chem. Biochem.* **1990**, *48*, 21. For a useful overview see: (c) Wagner, S. H.; Lundt, I. *J. Chem. Soc., Perkin Trans. 1* **2001**, 780−788.

(10) (a) Angelaud, R.; Landais, Y. *J. Org. Chem.* **1996**, *61*, 5202−5203. (b) Angelaud, R.; Landais, Y.; Schenk, K. *Tetrahedron Lett.* **1997**, *38*, 1407−1410. (c) Angelaud, R.; Landais, Y. *Tetrahedron Lett.* **1997**, *38*, 8841−8844. (d) Angelaud, R.; Landais, Y.; Parra-Rapado, L. *Tetrahedron Lett.* **1997**, *38*, 8845−8848. (e) Angelaud, R.; Babot, O.; Charvat, T.; Landais, Y. *J. Org. Chem.* **1999**, *64*, 9613−9624. (f) Landais, Y.; Zekri, E. *Tetrahedron Lett.* **2001**, *42*, 6547−6551. (g) Landais, Y.; Zekri, E. *Eur. J. Org. Chem.* **2002**, 4037−4053.

(11) (a) Roberson, C. W.; Woerpel, K. A. *Org. Lett.* **2000**, *2*, 621−623. (b) Roberson, C. W.; Woerpel, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 11342−11348.

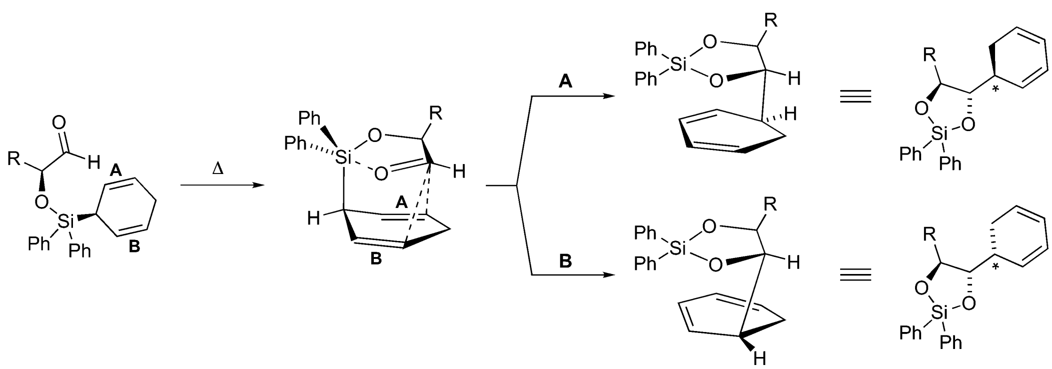
(12) (a) Ihara, M.; Suzuki, S.; Tokunaga, Y.; Fukumoto, K. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2811−2812. (b) Fujishima, H.; Takeshita, H.; Toyota, M.; Ihara, M. *Chem. Commun.* **1999**, 893−894. (c) Majo, V. J.; Suzuki, S.; Toyota, M.; Ihara, M. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3375−3381.

SCHEME 7[a]

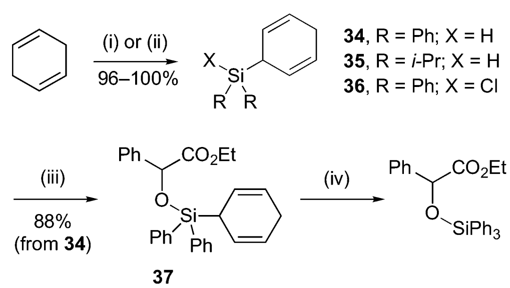


[a] Reagents: (i) O_3, CH_2Cl_2, then PPh_3; (ii) H_2, [Pd/C], EtOH; (iii) Ac_2O, pyridine, (DMAP); (iv) Amberlite IRA(OH) resin, MeOH.

SCHEME 8. Predicted Sense of Stereocontrol during Cyclohexadienyl Transfer Reactions

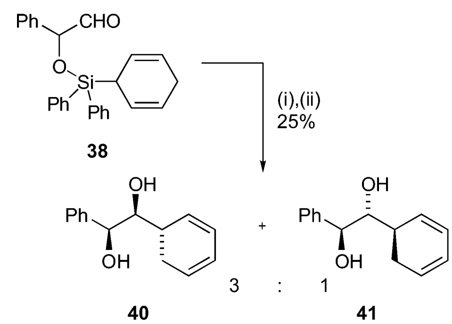


SCHEME 9[a]



[a] Reagents: (i) s-BuLi, TMEDA, THF, then Ph_2SiHCl; (ii) s-BuLi, TMEDA, THF, then i-Pr_2SiHCl; (iii) $CuCl_2$, CuI, THF; ethyl mandelate, Et_3N, DMAP, DMF; (iv) $PhCH_3$, 80−120 °C, 2−4 h.

SCHEME 10[a]



[a] Reagents: (i) $PhCH_3$, 120 °C, 20 h; (ii) KF, H_2O_2, aq. MeOH.

silanes could not be used directly to silylate α-hydroxyesters,[14] and we were unable to find a way to convert silane **35** into the corresponding chlorosilane in acceptable yield. Fortunately, application of Ishikawa's chlorination protocol[15] worked well with silane **34** (to give **36** in situ), and direct silylation of, for example, (±)-ethyl mandelate, under standard conditions, provided ester **37** in excellent yield. In a thermal stability test, heating this ester (**37**) resulted in complete conversion to ethyl *O*-(triphenylsilyl)mandelate within 2 h in d_8-toluene (NMR tube); however, degassing the solvent prior to heating effected a significant reduction in the rate of this process (<20% conversion after 5 h at 120 °C) to offer a potential window of stability within which to complete the silatropic ene process.

DIBAL reduction of ester **37** gave the aldehyde (**38**, Scheme 10) which was heated in degassed toluene, and the dioxasilolane **39** (not shown) cleaved to afford a 3:1 mixture of diastereomeric diols (**40** and **41**) in low overall yield. The stereochemistry of the major product (**40**) was established by X-ray crystallography,[16] the stereochemistry of the minor product (**41**) being assigned tentatively on the basis of the earlier results with (*Z*)-crotyl substrates. The low yield in this reaction was subsequently traced to oxidative side-reactions induced by the hydrogen peroxide that had been added in the cleavage step

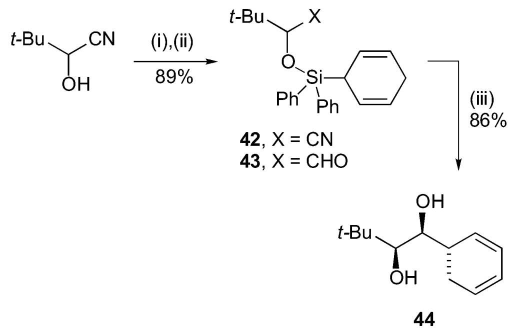
(13) (a) Schleth, F.; Studer, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 313−315. (b) Schleth, F.; Vogler, T.; Harms, K.; Studer, A. *Chem. Eur. J.* **2004**, *10*, 4171−4185.

(14) For example, application of Piers' protocol (ref 7a) to (*S*)-ethyl lactate and silane **34** led only to (*S*)-ethyl *O*-(phenyl)lactate in low yield.

(15) Kunai, A.; Kawakami, T.; Toyoda, E.; Ishikawa, M. *Organometallics* **1992**, *11*, 2708−2711.

(16) Crystal data for **40**: $C_{14}H_{16}O_2$, M = 216.28, colorless plates, orthorhombic, a = 8.4023(2), b = 16.1062(4), c = 17.4221(6) Å, V = 2357.72(11) Å^3, T = 150 K, space group *Pnaa*, Z = 8, μ(Mo Kα) = 0.08 mm^{-1}, 5322 reflections measured (R_{int} = 0.02), 1655 reflections used, final wR = 0.0664.

SCHEME 11[a]



[a] Reagents: (i) **36** (prepared *in situ* from **34**), Et_3N, DMAP, CH_2Cl_2; (ii) DIBAL, CH_2Cl_2; (iii) $PhCH_3$, 120 °C, 18 h, then TBAF, THF.

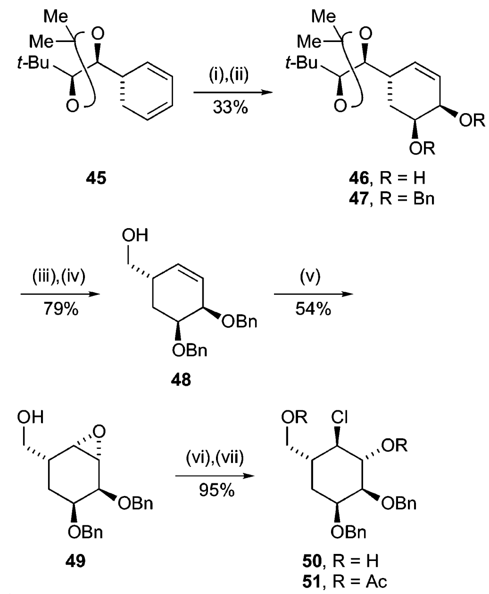
in order to aid separation of the phenylsilyl residues; in later work with different substrates the peroxide was omitted and yields improved.

It was expected that a directing group bulkier than phenyl would increase the stereoselectivity of the reaction, and a suitable substrate was prepared from pivalaldehyde cyanohydrin in an optimized procedure derived from our model studies (Scheme 11); important modifications included increasing the loading of CuI in the chlorination step and use of an excess of DMAP in dichloromethane in place of triethylamine/DMF for the silylation reaction. DIBAL reduction of silyl cyanohydrin **42** was efficient, paralleling our previous experience, and the silatropic ene substrate **43** was readily obtained on a gram scale. It was pleasing to find that this compound behaved exactly as expected on heating, the peroxide-free desilylation conditions affording diol **44** as a single diastereomer in high overall yield.

This diol was elaborated in two ways which differed in the nature of the first oxidation step. In the first route (Scheme 12), acetonide formation (→ **45**) was followed by regioselective dihydroxylation (of the alkene remote to the dioxolane), the low yield in this step (→ **46**) being attributed to double dihydroxylation and loss of the product during aqueous workup. Di-*O*-benzylation, acetonide hydrolysis, and diol cleavage with a reductive workup furnished cyclohexene derivative **48**. Interestingly, acidic treatment of the directed epoxidation product **49** and acetylation led to chloride **51** with essentially complete regiocontrol. Support for this structure was gained from a combination of NMR and MS experiments: $^1H-^1H$ COSY, coupling constant analysis, and an HMBC experiment established proton assignment and configuration around the ring (Figure 1), and HRMS established incorporation of Cl [found for $M(^{35}Cl)Na^+$ 478.1994]. This sense of regio- and stereocontrol may be a result of direct diaxial opening of the epoxide in the half-chair conformation that gives the chlorohydrin in conformation **50a** (Figure 2) which would relax to preferred conformation **50b**; however, diaxial opening of the epoxide in the alternative half-chair conformation would give chlorohydrin **52** which conceivably could rearrange, possibly during the acetylation, to give the same overall result.

As an alternative, singlet oxygen cycloaddition across diene **45** was used to initiate a reasonably efficient synthesis of tetra-*O*-benzyl *pseudo*-mannose (**60**, Scheme 13). Although the cycloaddition step was not usefully stereoselective, the major isomer (**53**) could be separated and elaborated by reduction, di-*O*-benzylation, dihydroxylation, a second di-*O*-benzylation, and hydrolysis to give hexa-ol derivative **59**. Diol cleavage with a reductive workup as before led to the mannose analogue **60** in good yield, in which the stereochemistry could be rigorously established (and that of the preceding intermediates inferred).

SCHEME 12[a]



[a] Reagents: (i) OsO_4, NMO, THF; (ii) NaH, BnBr, DMF; (iii) aq. TFA; (iv) $NaIO_4$, aq. THF, then $NaBH_4$, MeOH; (v) $VO(acac)_2$, t-BuOOH, CH_2Cl_2; (vi) aq. HCl, THF; (vii) Ac_2O, pyridine, DMAP.

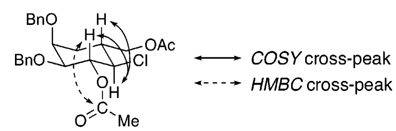


FIGURE 1. Diagnostic COSY and HMBC correlations in **51**.

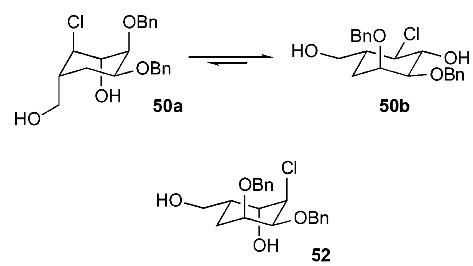
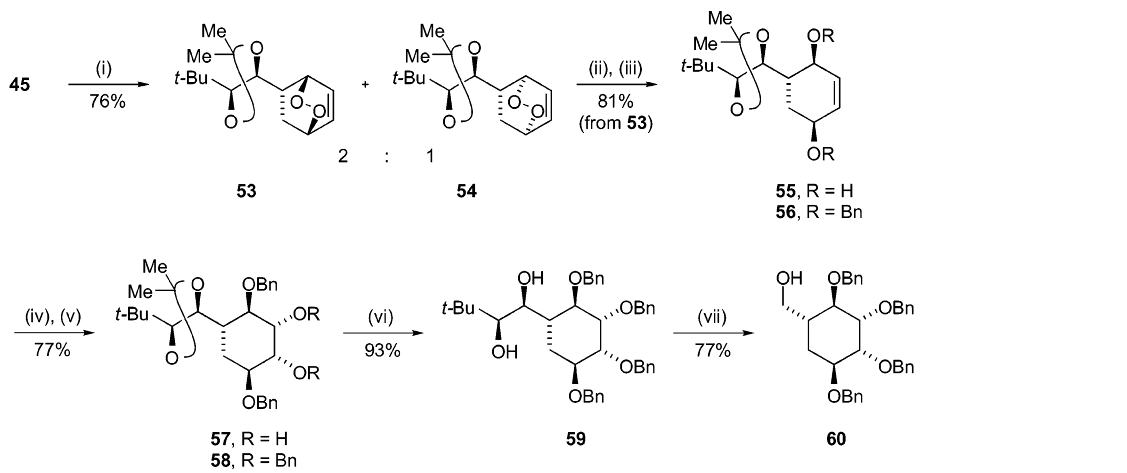


FIGURE 2. Plausible products from the acidolysis of epoxide **49**.

Conclusion

These silatropic carbonyl ene processes result in the products of functionalized allylation of α-hydroxyaldehydes with high stereospecificity and good, and predictable, stereoselectivity in favor of *syn*-diol products; furthermore, the reactions proceed thermally, in the absence of added Lewis acids, are tolerant of side-chain functionality, and the transferring group need not be a

SCHEME 13[a]



[a] Reagents: (i) O_2, methylene blue, CH_2Cl_2, hν; (ii) $LiAlH_4$, THF; (iii) NaH, BnBr, DMF; (iv) OsO_4, NMO, THF; (v) NaH, BnBr, DMF; (vi) aq. TFA; (vii) $NaIO_4$−SiO_2, THF, then $NaBH_4$, MeOH.

simple allylic unit. In addition to being of mechanistic interest, this methodology generates intermediates for elaboration into useful compounds including, as exemplified here, hydroxylated piperidines and carbasugars. We are currently establishing the scope of the process for accessing a variety of 1,2-dihydroxy-3-substituted-pent-4-enes.[17]

Experimental Section

(But-2-ynyl)diphenylsilane. To a stirred solution of 2-butyne (1.57 mL, 20.0 mmol) and TMEDA (3.0 mL, 20.0 mmol) in anhydrous tetrahydrofuran (20 mL) cooled to −78 °C was added *t*-BuLi (1.7 M in pentane, 12.4 mL, 21.0 mmol) dropwise, and the solution was stirred for 30 min at −78 °C and then warmed to RT over 30 min. The reaction mixture was recooled to −78 °C, and diphenylchlorosilane (3.90 mL, 20.0 mmol) was added. The resulting solution was stirred for 30 min at −78 °C and at RT for 1 h and then partitioned between water (50 mL) and ether (50 mL). The aqueous layer was extracted with ether (2 × 50 mL), and the combined organic fractions were washed with brine (100 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The resulting oil was purified by flash column chromatography (silica gel, petrol) to give the *title compound* as a colorless oil (4.52 g, 96%). R_f 0.18 (pentane). ν_{max}/cm^{-1} (thin film): 3069m, 3049m, 3011m, 2916m, 2880w, 2854w, 2134s, 1957w, 1915w, 1820w, 1588w, 1567w, 1486w, 1428s, 1395w, 1331w, 1303w, 1263w, 1179m, 1117s, 1066w, 1028w, 998w, 807s, 733s, 697s, 674s. δ_H (400 MHz, $CDCl_3$): 1.83 (3H, t, *J* 2.8, CH_3), 2.15 (2H, dq, *J* 3.2, 2.8, $SiCH_2$), 5.08 (1H, t, *J* 3.2, SiH), 7.39−7.55 (6H, m), and 7.72−7.74 (4H, m, 2 × Ph). δ_C (100.6 MHz, $CDCl_3$): 3.0, 3.6, 74.9, 75.7, 127.8, 129.9, 133.0, 135.2. *m/z* (EI$^+$): 236 (M$^+$, 18%), 221 (23), 183 (100), 158 (15), 105 (60), 53 (21). Accurate mass (EI$^+$): found, 236.1022; $C_{16}H_{16}Si$ (M$^+$) requires 236.1021. found, C 81.35, H 6.99; $C_{16}H_{16}Si$ requires C 81.30, H 6.82.

(*Z*-But-2-enyl)diphenylsilane. To a stirred solution of (but-2-ynyl)diphenylsilane (4.50 g, 19.1 mmol) was added DIBAL (1.0 M in heptane, 38.0 mL, 38.0 mmol), and the solution was heated at reflux for 5 h. The mixture was cooled to RT, poured into a mixture of dilute hydrochloric acid (1.0 M, 50 mL), ice (100 mL), and ether (100 mL), and stirred for 15 min. The layers were separated, and the aqueous phase was extracted with ether (2 × 100 mL); the combined organic fractions were washed successively with dilute hydrochloric acid (1.0 M, 2 × 100 mL), brine (100 mL), then dried ($MgSO_4$), and the solvents were removed in vacuo. The resulting oil was purified by flash column chromatography (silica gel, petrol) to give the *title compound* as a colorless oil (2.96 g, 65%). R_f 0.36 (petrol). ν_{max}/cm^{-1} (thin film): 3087m, 3069s, 3050m, 3017s, 2962m, 2926m, 2858m, 2125s, 1956w, 1883w, 1818w, 1766w, 1649m, 1589m, 1486m, 1428s, 1396m, 1362m, 1330w, 1302w, 1262w, 1152m, 1118s, 1066w, 1028w, 990m, 908s, 808s, 732s, 698s, 647m. δ_H (400 MHz, $CDCl_3$): 1.57 (3H, d, *J* 6.0, CH_3), 2.16 (2H, dd, *J* 8.0, 3.6, $SiCH_2$), 4.95 (1H, t, *J* 3.6, SiH), 5.45−5.65 (2H, m, CH=CH), 7.41−7.50 (6H, m), and 7.64−7.68 (4H, m, 2 × Ph). δ_C (100.6 MHz, $CDCl_3$): 12.7, 13.6, 123.4, 124.8, 128.0, 129.7, 134.1, 135.2. *m/z* (CI$^+$): 256 (MNH$_4^+$, 44%), 239 (MH$^+$, 16), 200 (100), 183 (96), 122 (14), 105 (36). Accurate mass (CI$^+$): found, 256.1520; $C_{16}H_{22}NSi$ (MNH$_4^+$) requires 256.1522.

(*S*)-Methyl *N*-(Benzyloxycarbonyl)[(but-3-enyl)diphenylsilanyloxy]isoserinate (7). To a stirred solution of but-3-enyl(diphenyl)silane[18] (934 mg, 3.92 mmol) and methyl (*S*)-*N*-(benzyloxycarbonyl)isoserinate (**5**)[19] (992 mg, 3.92 mmol) in anhydrous dichloromethane (4.0 mL), was added tris(pentafluorophenyl)borane (100 mg, 0.20 mmol), and the reaction mixture was heated at reflux for 16 h. The solution was allowed to cool to RT and then partitioned between water (50 mL) and ether (50 mL); the aqueous layer was separated and extracted with ether (2 × 25 mL). The combined organic extracts were washed with brine (50 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The resulting oil was purified by flash column chromatography (silica gel, 4:1 petrol/ether) to furnish the *title compound* (**7**) as a colorless syrup (1.34 g, 70%). R_f 0.26 (2:1 petrol/ether). $[\alpha]^{22}_D$ −16.2° (*c* 1.03, chloroform). ν_{max}/cm^{-1} (thin film): 3355m, 3070m, 3001m, 2951m, 1726s, 1638w, 1589w, 1515m, 1429m, 1244m, 1118s, 996m, 910w, 740m, 700s. δ_H (400 MHz, $CDCl_3$): 1.26−1.38 (2H, m, $SiCH_2$), 2.07−2.22 (2H, m, C*H*$_2$CH=), 3.54 (2H, app. t, *J* 5.6, NHC*H*$_2$), 3.58 (3H, s, OCH_3), 4.34 (1H, t, *J* 5.6, OCH), 4.91 (1H, dd, *J* 10.4, 1.6), and 5.00 (1H, dd, *J* 16.8, 1.6, CH=C*H*$_2$), 5.08 (2H, s, C*H*$_2$Ph), 5.11 (1H, br t, *J* 5.6, NH), 5.89 (1H, ddt, *J* 16.8, 10.4, 6.4, C*H*=CH$_2$), 7.26−7.50 (10H, m), and 7.56−7.60 (5H, m, 3 × Ph). δ_C (100.6 MHz, $CDCl_3$): 12.8, 26.8, 44.7, 52.0, 66.8, 71.3, 113.2, 128.0, 128.1, 128.5, 130.3, 133.4, 133.7, 134.8, 134.9, 136.4, 140.8, 156.0, 171.5. *m/z* (ES$^+$): 512 (MNa$^+$, 100%), 490 (MH$^+$, 22), 194 (20). Accurate mass (ES$^+$): found, 490.2050; $C_{28}H_{32}NO_5Si$ (MH$^+$) requires 490.2050.

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(*S*)-Methyl *N*-(Benzyloxycarbonyl)[(*E*-but-2-enyl)diphenylsilanyloxy]isoserinate (8). (1,5-Cyclooctadiene)bis(methyldiphenylphosphine)iridium(I) hexafluorophosphate (20.3 mg, 0.024 mmol) was dissolved in anhydrous dichloromethane (3.5 mL) and cooled to −78 °C. The Ir(I) catalyst was activated by passing hydrogen through the solution until the color changed from blood-red to colorless. The reaction vessel was purged with argon to remove any remaining hydrogen, and the solution was warmed to 0 °C. A solution of ester **7** (1.15 g, 2.35 mmol) in anhydrous dichloromethane (12.0 mL) was cooled to 0 °C and then added via cannula to the solution of preactivated catalyst. The resulting mixture was stirred at 0 °C, and the reaction progress was monitored by ^{1}H NMR. After 35 min the solvent was removed in vacuo; the resulting material was triturated with ether, the extracts filtered though a short plug of silica gel and Celite, and the solvents were removed from the filtrate in vacuo. The resulting oil was purified by flash column chromatography (silica gel, 4:1 petrol/ether) to furnish the *title compound* (**8**) as a colorless oil (1.15 g, 100%). R_f 0.44 (1:1 petrol/ether). $[\alpha]^{22}_D$ −10.3° (*c* 1.00, chloroform). ν_{max}/cm^{-1} (thin film): 3360m, 3070m, 3048m, 3015m, 2952m, 2884m, 2854w, 1754s, 1727s, 1590w, 1515s, 1429s, 1303m, 1245s, 1119s, 998m, 967m. δ_H (400 MHz, C_6D_6): 1.61 (3H, dd, *J* 6.2, 1.0, =CHC*H*$_3$), 2.30 (2H, d, *J* 8.0, SiCH_2), 3.27 (3H, s, OCH_3), 3.61 (2H, app. t, *J* 5.6, NHC*H*$_2$), 4.52 (1H, t, *J* 5.6, OCH), 4.98 (1H, t, *J* 5.6, NH), 5.11 and 5.16 (2 × 1H, 2 × d, *J* 12.0, C*H*$_2$Ph), 5.42−5.52 and 5.59−5.69 (2 × 1H, 2 × m, CH=CH), 7.25−7.34 (10H, m), and 7.78−7.81 (5H, m, 3 × Ph). δ_C (100.6 MHz, C_6D_6): 18.4, 20.5, 45.3, 51.6, 66.9, 72.1, 125.2, 126.4, 128.4−128.8 (overlapping), 130.5, 134.7 (two peaks), 135.6, 135.8, 137.5, 156.5, 171.6. *m/z* (ES$^+$): 512 (MNa$^+$, 90%), 507 (MNH$_4^+$, 40), 490 (MH$^+$, 14), 434 (100), 412 (17). Accurate mass (ES$^+$): found, 512.1862; $C_{28}H_{31}NO_5Si$ (MNa$^+$) requires 512.1869.

(*S*)-Methyl *N*-(Benzyloxycarbonyl)[(*Z*-but-2-enyl)diphenylsilanyloxy]isoserinate (9). To a stirred solution of ((*Z*)-but-2-enyl)diphenylsilane (1.05 g, 4.41 mmol) and methyl (*S*)-*N*-(benzyloxycarbonyl)isoserinate (**5**)[19] (1.11 g, 4.39 mmol) in anhydrous dichloromethane (4.5 mL) was added tris(pentafluorophenyl)borane (112 mg, 0.22 mmol), and the reaction mixture was heated at reflux for 16 h. The solution was allowed to cool to RT and then partitioned between water (50 mL) and ether (50 mL); the aqueous layer was separated and extracted with ether (2 × 25 mL). The combined organic extracts were washed with brine (50 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The resulting oil was purified by flash column chromatography (silica gel, 4:1 petrol/ether) to furnish the *title compound* (**9**) as a colorless syrup (1.65 g, 77%). R_f 0.35 (1:1 petrol/ether). $[\alpha]^{22}_D$ −13.6° (*c* 1.07, chloroform). ν_{max}/cm^{-1} (thin film): 3427m, 3070m, 3049m, 3017m, 2952m, 1725s, 1650w, 1590w, 1515s, 1455m, 1429s, 1396w, 1364w, 1332w, 1215s, 1119s, 991m, 910w, 781m, 737s, 700s, 648m. δ_H (400 MHz, $CDCl_3$): 1.45 (3H, d, *J* 5.6, =CHC*H*$_3$), 2.20 (2H, d, *J* 7.6, SiCH_2), 3.56 (2H, app. t, *J* 5.6, NHC*H*$_2$), 3.58 (3H, s, CO_2CH_3), 4.39 (1H, t, *J* 5.6, OCH), 5.08 and 5.11 (2 × 1H, 2 × d, *J* 13.0, C*H*$_2$Ph), 5.15 (1H, br t, *J* 5.6, N*H*), 5.37−5.53 (2H, m, CH=CH), 7.30−7.46 (10H, m), and 7.55−7.63 (5H, m, 3 × Ph). δ_C (100.6 MHz, $CDCl_3$): 12.6, 15.3, 44.8, 52.0, 66.9, 71.5, 123.4, 124.1, 127.9, 128.1, 128.5, 129.5, 130.2, 133.5, 134.8, 136.4, 156.2, 171.5. *m/z* (ES$^+$): 512 (MNa$^+$, 100%), 507 (MNH$_4^+$, 27). Accurate mass (ES$^+$): found, 507.2322; $C_{28}H_{35}N_2O_5Si$ (MNH$_4^+$) requires 507.2315.

(*S*)-Methyl *N*-(Benzyloxycarbonyl)[(3-methylbut-2-enyl)di(isopropyl)silanyloxy]isoserinate. To a stirred solution of (3-methylbut-2-enyl)di(isopropyl)silane[6] (500 mg, 2.71 mmol) and methyl (*S*)-*N*-(benzyloxycarbonyl)isoserinate (**5**)[19] (617 mg, 2.44 mmol) in anhydrous toluene (10.0 mL) was added tris(pentafluorophenyl)borane (123 mg, 0.24 mmol), and the reaction mixture was heated at reflux for 24 h. The solution was allowed to cool to RT and then partitioned between water (50 mL) and ether (50 mL); the aqueous layer was separated and extracted with ether (2 × 25 mL). The combined organic extracts were washed with brine (25 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The crude product was purified by flash column chromatography (silica gel, 4:1 petrol/ether) to yield the *title compound* as a colorless syrup (120 mg, 11%). R_f 0.37 (1:1 petrol/ether). $[\alpha]^{20}_D$ −6.60° (*c* 1.00, chloroform). ν_{max}/cm^{-1} (thin film): 3361m, 3033w, 2946s, 2867s, 1761s, 1729s, 1514m, 1456m, 1376w, 1248m, 1143s, 1097w, 995m, 883m, 844w, 814w, 748s, 697m. δ_H (400 MHz, $CDCl_3$): 1.03−1.14 (14H, m, 2 × *i*-Pr), 1.58 (2H, d, *J* 8.0, SiCH_2) overlain by 1.60 and 1.67 (2 × 3H, 2 × s, =C(CH_3)$_2$), 3.46−3.59 (2H, m, NHC*H*$_2$), 3.72 (3H, s, OCH_3), 4.40 (1H, t, *J* 5.0, OCH), 5.08 and 5.13 (2 × 1H, 2 × d, *J* 12.4, C*H*$_2$Ph) overlaying 5.11−5.18 (2H, m, CH= and NH), 7.27−7.39 (5H, m, Ph). δ_C (100.6 MHz, $CDCl_3$): 12.4, 12.7, 17.3 (two peaks), 17.4, 17.6, 25.8, 45.1, 52.0, 66.8, 71.1, 118.4, 128.1, 128.5, 130.0, 136.4, 156.2, 172.0. *m/z* (CI$^+$): 453 (MNH$_4^+$, 100%), 436 (MH$^+$, 13). Accurate mass (ES$^+$): found, 453.2786; $C_{23}H_{41}N_2O_5Si$ (MNH$_4^+$) requires 453.2785.

(*S*)-*N*-(Benzyloxycarbonyl)[(3-methylbut-2-enyl)di(isopropyl)silanyloxy]isoserinal (11). To a stirred solution of (*S*)-methyl *N*-(benzyloxycarbonyl)[(3-methylbut-2-enyl)di(isopropyl)silanyloxy]isoserinate (83 mg, 0.19 mmol) in anhydrous dichloromethane (2.0 mL) cooled to −78 °C was added DIBAL (1.0 M in dichloromethane, 290 μL, 0.29 mmol) dropwise, and the solution was stirred at −78 °C for 1 h. The reaction was quenched by the addition of a saturated solution of tartaric acid in methanol (1 mL). The mixture was warmed to RT and partitioned between aqueous tartaric acid solution (30% w/v, 15 mL) and ether (15 mL). The aqueous layer was extracted with ether (3 × 15 mL), and the combined organic extracts were washed with brine (25 mL), dried (Na_2SO_4), and the solvents were removed in vacuo. The crude product was purified by flash column chromatography (silica gel, 8:1 petrol/ethyl acetate) to furnish *aldehyde* **11** as a colorless syrup (60 mg, 78%). R_f 0.63 (ether [streaks]). $[\alpha]^{20}_D$ −1.90° (*c* 1.00, chloroform). ν_{max}/cm^{-1} (thin film): 3349m, 3066w, 3034w, 2944s, 2892m, 2867s, 1732s, 1517m, 1456m, 1403w, 1377w, 1347w, 1328w, 1256s, 1153s, 1128s, 1098m, 1002m, 920w, 883m, 844w, 815w, 775w, 747m, 697m. δ_H (400 MHz, $CDCl_3$): 0.98−1.14 (14H, m, 2 × *i*-Pr), 1.59 and 1.67 (2 × 3H, 2 × s, =C(CH_3)$_2$) overlays 1.60 (2H, m, SiCH_2), 3.42 (1H, app. dt, *J* 14.0, 5.0) and 3.58 (1H, ddd, *J* 14.0, 7.2, 5.0, NHC*H*$_2$), 4.18 (1H, t, *J* 5.0, OCH), 5.08 and 5.12 (2 × 1H, 2 × d, *J* 12.0, C*H*$_2$Ph), 5.12−5.19 (2H, m, CH= and NH), 7.30−7.39 (5H, m, Ph), 9.62 (1H, s, C*H*O). δ_C (100.6 MHz, $CDCl_3$): 12.4, 12.6 (two peaks), 17.3, 17.4, 17.7, 25.8, 43.0, 66.9, 76.3, 118.2, 128.1, 128.2, 128.5, 130.4, 136.3, 156.2, 202.2. *m/z* (CI$^+$): 423 (MNH$_4^+$, 29%), 406 (MH$^+$, 91), 366 (13), 336 (100), 315 (49), 272 (30), 218 (21), 169 (35), 148 (75), 108 (25). Accurate mass (ES$^+$): found, 423.2680; $C_{22}H_{39}N_2O_4Si$ (MNH$_4^+$) requires 423.2679.

(*S*)-*N*-(Benzyloxycarbonyl)[(*E*-but-2-enyl)diphenylsilanyloxy]isoserinal (12). To a stirred solution of silyl isoserinate **8** (1.14 g, 2.33 mmol) in anhydrous dichloromethane (23.0 mL) cooled to −78 °C was added DIBAL (1.0 M in dichloromethane, 3.50 mL, 3.50 mmol) dropwise, and the solution was stirred at −78 °C for 2 h. The reaction was quenched by the addition of a saturated solution of tartaric acid in methanol (5 mL). The mixture was warmed to RT and partitioned between aqueous tartaric acid solution (30% w/v, 50 mL) and ether (25 mL). The aqueous layer was extracted with ether (3 × 25 mL), and the combined organic extracts were washed with brine (50 mL), dried (Na_2SO_4), and the solvents were removed in vacuo. The crude product was purified by flash column chromatography (silica gel, 3:1 petrol/ether) to furnish *aldehyde* **12** as a colorless syrup (537 mg, 50%). R_f 0.21 (1:1 petrol/ether [streaks]). $[\alpha]^{22}_D$ +1.27° (*c* 1.02, chloroform). ν_{max}/cm^{-1} (thin film): 3423m, 3069m, 3049m, 3014m, 2932m, 2854w, 1722s, 1517s, 1454w, 1428m, 1258m, 1153m, 1118s, 998w, 968w, 910w, 739s, 700s. δ_H (500 MHz, C_6D_6): 1.48 (3H, d, *J* 6.5, =CHC*H*$_3$), 2.06−2.15 (2H, m, SiCH_2), 3.15 and 3.28 (2 × 1H, 2 × app. dt, *J* 14.0, 5.5, NHC*H*$_2$), 3.97 (1H, t, *J* 5.5, OCH), 4.58 (1H, t, *J* 5.5, NH), 4.96 and 5.02 (2 ×

1H, 2 × d, *J* 12.5, CH_2Ph), 5.32 (1H, dq, *J* 15.8, 6.5, CH=C*H*CH_3), 5.46 (1H, dt, *J* 15.8, 8.0, C*H*=CHCH_3), 7.16−7.25 (10H, m), and 7.54−7.72 (5H, m, 3 × Ph), 9.27 (1H, s, CHO). δ_C (125.7 MHz, C_6D_6): 18.5, 20.5, 43.0, 67.2, 77.6, 125.0, 126.8, 128.1−135.5 (overlapping), 134.6, 137.5, 156.6, 200.2. *m/z* (ES^+): 477 (MNH_4^+, 100%), 460 (MH^+, 73). Accurate mass (ES^+): found, 460.1946; $C_{27}H_{30}NO_4Si$ (MH^+) requires 460.1944.

(*S*)-*N*-(Benzyloxycarbonyl)[(*Z*-but-2-enyl)diphenylsilanyloxy]isoserinal (13). To a stirred solution of silyl isoserinate **9** (1.01 g, 2.07 mmol) in anhydrous dichloromethane (20.0 mL) cooled to −78 °C was added DIBAL (1.0 M in dichloromethane, 3.10 mL, 3.10 mmol) dropwise, and the solution was stirred at −78 °C for 1.5 h. The reaction was quenched by the addition of a saturated solution of tartaric acid in methanol (5 mL). The mixture was warmed to RT and partitioned between aqueous tartaric acid solution (30% w/v, 50 mL) and ether (25 mL). The aqueous layer was extracted with ether (3 × 25 mL), and the combined organic extracts were washed with brine (50 mL), dried (Na_2SO_4), and the solvents were removed in vacuo. The crude product was purified by flash column chromatography (silica gel, 3:1 petrol/ether) to furnish *aldehyde* **13** as a colorless syrup (720 mg, 76%). R_f 0.28 (1:1 petrol/ether [streaks]). $[\alpha]^{22}_D$ −1.67° (*c* 1.02, chloroform). ν_{max}/cm^{-1} (thin film): 3425s, 3070m, 3049m, 3017m, 2935m, 2858w, 1704s, 1650w, 1590w, 1515s, 1455m, 1429s, 1394w, 1363w, 1331w, 1257s, 1152s, 1117s, 1027w, 990m, 911m, 857w. δ_H (400 MHz, $CDCl_3$): 1.46 (3H, d, *J* 6.0, =CHCH_3), 2.19−2.29 (2H, m, SiCH_2), 3.45 and 3.59 (2 × 1H, 2 × app. dt, *J* 14.4, 5.2, NHCH_2), 4.26 (1H, t, *J* 5.2, OCH), 5.06−5.08 (1H, m, N*H*) overlaying 5.07 and 5.11 (2 × 1H, 2 × d, *J* 12.4, CH_2Ph), 5.40−5.56 (2H, m, C*H*=C*H*), 7.32−7.49 (10H, m), and 7.63−7.69 (5H, m, 3 × Ph), 9.59 (1H, s, CHO). δ_C (100.6 MHz, $CDCl_3$): 12.7, 15.3, 42.6, 66.9, 123.2, 124.4, 127.9, 128.1, 128.2, 128.5, 130.5, 133.3, 133.4, 134.8, 136.3, 156.2, 201.0. *m/z* ($APCI^+$): 460 (MH^+, 35%), 416 (29), 404 (16), 360 (35), 253 (50), 246 (22), 192 (99), 180 (18), 120 (100), 105 (12). Accurate mass (ES^+): found, 460.1943; $C_{27}H_{30}NO_4Si$ (MH^+) requires 460.1944.

(3*S*,4*S*)-3-[(Benzyloxycarbonyl)amino]methyl-4-(1,1-dimethylprop-2-enyl)-2,5-dioxa-1,1-di(isopropyl)-silolane (15). A solution of aldehyde **11** (49 mg, 0.12 mmol) in toluene-d_8 (600 μL) was heated at 120 °C in a sealed NMR tube, and the reaction progress was monitored by ^{1}H NMR. After 30 h the mixture was cooled to RT, and the solvent was removed in vacuo. Purification by flash column chromatography (silica gel, 5:1 petrol/ether) gave *dioxasilolane* **15** as a colorless oil (45 mg, 91%). R_f 0.58 (1:1 petrol/ether). $[\alpha]^{22}_D$ −33.1° (*c* 0.55, chloroform). ν_{max}/cm^{-1} (thin film): 3338m, 2946s, 2867s, 1724s, 1513m, 1465m, 1382w, 1248m, 1148w, 1073m, 1041m, 918w, 883w, 849w, 797w, 752w, 696m. δ_H (400 MHz, $CDCl_3$): 1.00−1.08 (20H, m, 2 × *i*-Pr and CMe_2), 3.02 (1H, ddd, *J* 13.0, 8.0, 3.8, NHC*H*H′), 3.42 (1H, d, *J* 8.0, C*H*(O)-CMe_2), 3.60 (1H, ddd, *J* 13.0, 8.0, 2.8, NHCH*H′*), 3.84 (1H, td, *J* 8.0, 2.8, CH_2C*H*O), 5.02−5.14 (4H, m, CH=CH_2 and CH_2-Ph), 5.23−5.30 (1H, m, NH), 5.90 (1H, dd, *J* 17.6, 10.8, C*H*=CH_2), 7.31−7.39 (5H, m, Ph). δ_C (100.6 MHz, $CDCl_3$): 12.5, 12.7, 16.8 (two peaks), 16.9, 22.6, 24.0, 40.6, 46.7, 66.7, 75.5, 83.8, 113.2, 128.1, 128.5, 136.5, 143.9, 156.3. *m/z* ($APCI^+$): 406 (MH^+, 46%), 363 (100), 280 (10), 255 (10), 122 (10). Accurate mass (ES^+): found, 406.2408; $C_{22}H_{36}NO_4Si$ (MH^+) requires 406.2413.

(2*S*,3*S*)-1-(Benzyloxycarbonyl)amino-4,4-dimethylhex-5-en-2,3-diol (16). To a stirred solution of dioxasilolane **15** (41 mg, 0.10 mmol) in methanol (1.0 mL) was added KF (17 mg, 0.30 mmol), and the reaction mixture was stirred at RT for 16 h. The solvent was removed in vacuo; the crude residue was triturated with ether, and the combined extracts were filtered through Celite, the solvents were removed in vacuo. The crude product was purified by flash column chromatography (silica gel, 1:2 petrol/ether) to give *aminodiol* **16** as a colorless glassy solid (26 mg, 88%). R_f 0.49 (ether). $[\alpha]^{22}_D$ −10.9° (*c* 1.01, chloroform). ν_{max}/cm^{-1} (KBr disk): 3428s, 3399s, 3084w, 3034w, 2946m, 1694s, 1638w, 1538m, 1455m, 1415m, 1271s, 1145m, 1106m, 1012m, 914m, 844w, 824w, 736m, 697s. δ_H (400 MHz, DMSO-d_6): 0.95 and 0.96 (2 × 3H, 2 × s, CMe_2), 2.97 (2H, app. t, *J* 6.0, NHCH_2), 3.03 (1H, d, *J* 8.2, C*H*(OH)CMe_2), 3.60 (1H, app. q, app. *J* 6.8, CH_2C*H*(OH)), 4.17 (1H, d, *J* 8.2, CH(O*H*)CMe_2), 4.36 (1H, d, *J* 7.2, CH_2CH(O*H*)), 4.90−5.03 (4H, m, CH=CH_2 and CH_2Ph), 5.87 (1H, dd, *J* 17.6, 10.8, C*H*=CH_2), 7.20 (1H, br t, *J* 6.0, NH), 7.29−7.38 (5H, m, Ph). δ_C (100.6 MHz, DMSO-d_6): 22.0, 24.9, 41.2, 45.3, 65.1, 67.6, 75.3, 111.3, 127.7, 127.8, 128.4, 137.3, 146.4, 156.3. *m/z* ($APCI^+$): 294 (MH^+, 16%), 250 (100), 160 (21), 142 (40), 104 (18). Accurate mass (ES^+): found, 294.1708; $C_{16}H_{24}NO_4$ (MH^+) requires 294.1705.

Alternative Procedure from Aldehyde 10. A stirred solution of aldehyde **10**[6] (743 mg, 1.57 mmol) in anhydrous toluene (8.0 mL) was heated at 120 °C in a base-washed sealed tube. After 20 h the reaction mixture was cooled to RT and the solvent was removed in vacuo to furnish *siladioxolane* **14** (unstable toward chromatography and taken on directly into the oxidation reaction). R_f 0.83 (ether). δ_H (400 MHz, toluene-d_8): 1.06 (6H, s, CMe_2), 3.15 (1H, dt, *J* 14.0, 6.4) and 3.42 (1H, ddd, *J* 14.0, 6.4, 3.2, NHCH_2), 3.80 (1H, d, *J* 6.4, C*H*(O)CMe_2), 4.20 (1H, td, *J* 6.4, 3.2, CH_2C*H*O), 4.90 (1H, t, *J* 6.4, NH), 4.94−5.12 (4H, m, CH=CH_2 and CH_2Ph), 5.90 (1H, dd, *J* 17.4, 11.0, C*H*=CH_2), 6.93−7.33 (11H, m), and 7.61−7.72 (4H, m, Ph). δ_C (100.6 MHz, toluene-d_8): 22.8, 24.1, 41.6, 47.4, 67.1, 77.0, 84.8, 114.0, 128.1, 128.5, 128.7, 128.9, 129.0, 132.4, 133.5, 135.4, 135.6, 135.8, 135.9, 137.9, 144.2, 156.9. *m/z* ($APCI^+$): 474 (MH^+, 100%), 430 (81), 396 (77), 352 (60), 306 (84), 262 (58), 160 (60), 122 (36). The crude product was dissolved in methanol (15.0 mL); then, KF (274 mg, 4.72 mmol) and H_2O_2 (35% in water, 1.5 mL) were added, and the reaction mixture was stirred at RT for 3 h. The solvent was removed in vacuo; the crude residue was triturated with ether, the combined extracts were filtered through Celite, and the filtrate was concentrated in vacuo. Purification by flash column chromatography (silica gel, 1:2 petrol/ether) afforded *aminodiol* **16** as a colorless glassy solid (447 mg, 95%). Data as above.

(2*S*,3*S*,4*R*)-1-(Benzyloxycarbonyl)amino-4-methylhex-5-en-2,3-diol (18). A stirred solution of aldehyde **12** (419 mg, 0.91 mmol) in anhydrous toluene (4.5 mL) was heated at 130 °C in a base-washed sealed tube. After 17 h the reaction mixture was cooled to RT, and the solvent was removed in vacuo. The crude siladioxolane (**17**) was dissolved in methanol (9.0 mL); KF (159 mg, 2.74 mmol) and H_2O_2 (35% in water, 1.0 mL) were added, and the reaction mixture was stirred at RT for 4 h. The solvent was removed in vacuo; the crude residue was triturated with ether, the combined extracts were filtered through Celite, and the filtrate was concentrated in vacuo. The crude product was purified by flash column chromatography (silica gel, 1:1 petrol/ether) to give *aminodiol* **18** as a colorless crystalline solid (205 mg, 80%). R_f 0.27 (ether). M.p. 82−85 °C (ether). $[\alpha]^{22}_D$ −3.00° (*c* 1.01, chloroform). ν_{max}/cm^{-1} (KBr disk): 3456m, 3343m, 2974m, 2951m, 2906m, 1671s, 1552s, 1441m, 1350m, 1277s, 1131s, 1054m, 1036m, 916m, 780w, 750m. δ_H (400 MHz, DMSO-d_6): 1.00 (3H, d, *J* 6.4, CH_3), 2.31−2.41 (1H, m, C*H*Me), 3.01−3.10 (3H, m, NHCH_2 and C*H*(OH)CHMe), 3.52 (1H, ddt, *J* 13.6, 6.8, 2.0, CH_2C*H*(OH)), 4.18 (1H, d, *J* 8.0, CH(O*H*)CHMe), 4.37 (1H, d, *J* 6.8, CH_2CH(O*H*)), 4.90−5.09 (4H, m, CH=CH_2 and CH_2Ph), 5.71 (1H, ddd, *J* 17.2, 10.2, 8.0, C*H*=CH_2), 7.11 (1H, t, *J* 5.6, NH), 7.30−7.40 (5H, m, Ph). δ_C (100.6 MHz, DMSO-d_6): 17.3, 41.1, 45.1, 66.0, 70.1, 74.9, 115.1, 128.6, 129.2, 138.1, 142.8, 157.2. *m/z* (ES^+): 302 (MNa^+, 100%), 280 (MH^+, 37), 236 (81). Accurate mass (ES^+): found, 302.1371; $C_{15}H_{21}NO_4Na$ (MNa^+) requires 302.1368.

(2*S*,3*S*,4*S*)-1-(Benzyloxycarbonyl)amino-4-methylhex-5-en-2,3-diol (20). A stirred solution of aldehyde **13** (490 mg, 1.07 mmol) in anhydrous toluene (5.5 mL) was heated at 130 °C in a base-washed sealed tube. After 24 h the reaction mixture was cooled to RT, and the solvent was removed in vacuo to furnish the crude siladioxolane (**19**) which was dissolved in methanol (10.5 mL); KF (187 mg, 3.22 mmol) and H_2O_2 (35% in water, 1.0 mL) were added, and the reaction mixture was stirred at RT for 14 h. The solvent was removed in vacuo; the crude residue was triturated with ether, the combined extracts were filtered through Celite, and the filtrate was concentrated in vacuo. The crude product was purified by flash column chromatography (silica gel, 1:1 petrol/ether) to give *aminodiol* **20** as a colorless crystalline solid (233 mg, 78%). R_f 0.24 (ether). M.p. 77−79 °C (ether). $[\alpha]^{22}_D$ −19.4° (*c* 1.08, chloroform). ν_{max}/cm^{-1} (KBr disk): 3481m, 3348m, 3066m, 3034m, 2980m, 2932m, 2884m, 1672s, 1643m, 1548s, 1440m, 1276s, 1109m, 1034m, 906m, 752m. δ_H (400 MHz, DMSO-d_6): 0.92 (3H, d, *J* 7.2, CH_3), 2.33 (1H, app. sextet, app. *J* 7.0, C*H*Me), 2.98−3.14 (3H, m, NHCH_2 and C*H*(OH)CHMe), 3.49 (1H, ddt, *J* 10.8, 6.4, 3.6, CH_2C*H*(OH)), 4.22 (1H, d, *J* 6.8, CH-(O*H*)CHMe), 4.49 (1H, d, *J* 6.4, CH_2CH(O*H*)), 4.90−5.05 (4H, m, CH=CH_2 and CH_2Ph), 5.89 (1H, ddd, *J* 17.6, 10.0, 7.2, C*H*=CH_2), 7.11 (1H, t, *J* 5.6, NH), 7.29−7.38 (5H, m, Ph). δ_C (100.6 MHz, DMSO-d_6): 17.5, 40.6, 44.7, 66.0, 70.4, 75.2, 114.6, 128.5, 129.2, 138.1, 142.9, 157.2. *m/z* (ES$^+$): 302 (MNa$^+$, 100%), 280 (MH$^+$, 33), 236 (82). Accurate mass (ES$^+$): found, 302.1363; $C_{15}H_{21}NO_4Na$ (MNa$^+$) requires 302.1368. Also obtained was *(2*S*,3*R*,4*R*)-1-(benzyloxycarbonyl)amino-4-methylhex-5-en-2,3-diol* (**21**) as a colorless semisolid (22 mg, 7%). R_f 0.33 (ether). $\alpha]^{22}_D$ +17.5° (*c* 0.49, chloroform). ν_{max}/cm^{-1} (KBr disk): 3400s, 3338s, 3069m, 3037m, 3000m, 2958m, 2928m, 2869m, 1667s, 1547s, 1440m, 1367w, 1282m, 1149w, 1071m, 1011w, 971w, 919w. δ_H (400 MHz, DMSO-d_6): 0.99 (3H, d, *J* 7.2, CH_3), 2.48−2.55 (1H, m, C*H*Me), 2.92 (1H, ddd, *J* 13.2, 8.2, 5.6, NHC*H*H′) 3.11 (1H, ddd, *J* 8.2, 6.0, 2.8, C*H*(OH)CHMe), 3.30 (1H, ddt, *J* 8.2, 6.4, 2.8, CH_2C*H*(OH)), 3.37 (1H, ddd, *J* 13.2, 5.6, 2.8, NHCH*H*′), 4.58 (1H, d, *J* 6.4, CH_2CH(O*H*)), 4.63 (1H, d, *J* 6.0, CH(O*H*)CHMe), 4.93−5.05 (4H, m, CH=CH_2 and CH_2Ph), 5.80 (1H, ddd, *J* 17.2, 10.4, 8.4, C*H*=CH_2), 6.95 (1H, t, *J* 5.6, NH), 7.30−7.37 (5H, m, Ph). δ_C (100.6 MHz, DMSO-d_6): 18.5, 39.6, 45.4, 66.1, 71.5, 76.4, 115.6, 128.6, 129.2, 138.5, 141.2, 157.3. *m/z* (ES$^+$): 302 (MNa$^+$, 100%), 280 (MH$^+$, 25), 236 (60). Accurate mass (ES$^+$): found, 302.1371; $C_{15}H_{21}NO_4Na$ (MNa$^+$) requires 302.1368.

General Procedure for Corey−Winter Diene Synthesis. To a stirred solution of the diol (0.10 mmol) in anhydrous tetrahydrofuran (2.0 mL) was added 1,1-thiocarbonyldiimidazole (0.20 mmol), and the mixture was heated at reflux. After 20 h the reaction mixture was cooled to RT, and the solvent was removed in vacuo. The crude thiocarbonate was purified by flash column chromatography (silica gel, 3:2 petrol/ether) and was then dissolved in triethyl phosphite (2.0 mL) and heated at reflux. After 2.5 h the reaction mixture was cooled to RT, and the solvent was removed in vacuo. The residual oil was azeotroped with toluene (3 × 5 mL), and the diene was purified by flash column chromatography (silica gel, 9:1 petrol/ether).

1-(Benzyloxycarbonyl)amino-4,4-dimethylhexa-2(*E*),5-diene (22). With the use of the general procedure, *diene* **22** was obtained as a colorless oil (76% from diol **16**). R_f 0.55 (1:1 petrol/ether). ν_{max}/cm^{-1} (thin film): 3336m, 3066w, 3034w, 2963m, 2869w, 1702s, 1529m, 1456w, 1360w, 1246s, 1135m, 975m, 914m. δ_H (400 MHz, $CDCl_3$): 1.10 (6H, s, CMe_2), 3.80 (2H, br t, *J* 6.0, NHCH_2), 4.76 (1H, br s, N*H*), 4.94 (1H, dd, *J* 10.8, 1.2) and 4.95 (1H, dd, *J* 17.2, 1.2, CH=CH_2), 5.12 (2H, s, CH_2Ph), 5.41 (1H, dt, *J* 15.8, 6.0, CH_2C*H*=), 5.61 (1H, dt, *J* 15.8, 1.2, =C*H*CMe_2), 5.80 (1H, dd, *J* 17.2, 10.8, C*H*=CH_2), 7.30−7.39 (5H, m, Ph). δ_C (100.6 MHz, $CDCl_3$): 26.8, 39.0, 43.1, 66.7, 110.9, 122.6, 128.1, 128.5, 136.6, 141.4, 146.7, 156.8. *m/z* (APCI$^+$): 260 (MH$^+$, 29%), 215 (44), 199 (100), 156 (27), 151 (87). Accurate mass (CI$^+$): found, 260.1649; $C_{16}H_{22}NO_2$ (MH$^+$) requires 260.1651. Data for the intermediate thiocarbonate, *(4*S*,5*S*)-5-[(benzyloxycarbonyl)amino]methyl-4-(1,1-dimethylprop-2-enyl)-1,3-dioxolane-2-thione*, a colorless oil, are as follows. R_f 0.62 (ether). $[\alpha]^{22}_D$ +15.4° (*c* 1.51, chloroform). ν_{max}/cm^{-1} (thin film): 3337s, 3088w, 3034w, 2971m, 1704s, 1520s, 1455m, 1282s, 1166s, 1092w, 1049m, 978s, 929m. δ_H (400 MHz, $CDCl_3$): 1.13 and 1.14 (2 × 3H, 2 × s, CMe_2), 3.44−3.56 (2H, m, NHCH_2), 4.41 (1H, d, *J* 6.0, C*H*(OR)CMe_2), 4.64 (1H, td, *J* 6.0, 4.4, CH_2C*H*O), 5.10 and 5.16 (2 × 1H, 2 × d, *J* 12.4, CH_2Ph), 5.20 (1H, d, *J* 17.6) and 5.25 (1H, d, *J* 10.4, CH=CH_2) overlaying 5.21 (1H, t, *J* 6.4, N*H*), 5.74 (1H, dd, *J* 17.6, 10.4, C*H*=CH_2), 7.31−7.40 (5H, m, Ph). δ_C (100.6 MHz, $CDCl_3$): 21.5, 22.6, 39.9, 43.4, 67.4, 81.9, 89.7, 116.7, 128.1, 128.4, 128.6, 135.8, 139.6, 153.2, 156.7. *m/z* (ES$^+$): 358 (MNa$^+$, 29%), 336 (MH$^+$, 100), 209 (28). Accurate mass (ES$^+$): found, 336.1270; $C_{17}H_{22}NO_4S$ (MH$^+$) requires 336.1270.

(4*R*)-1-(Benzyloxycarbonyl)amino-4-methylhex-2(*E*),5-diene (23). With the use of the general procedure, *diene* **23** was obtained as a colorless oil (91% from diol **18**). R_f 0.62 (1:1 petrol/ether). $[\alpha]^{22}_D$ −6.58° (*c* 0.73, chloroform). ν_{max}/cm^{-1} (thin film): 3336m, 3033w, 2964m, 2922m, 1703s, 1530m, 1455m, 1363w, 1250s, 1134w, 1046w, 972m. δ_H (400 MHz, $CDCl_3$): 1.09 (3H, d, *J* 7.2, CH_3), 2.80−2.91 (1H, m, C*H*Me), 3.80 (2H, t, *J* 5.6, NHCH_2), 4.77 (1H, br s, NH), 4.95−4.99 (2H, m, CH=CH_2), 5.12 (2H, s, CH_2Ph), 5.46 (1H, dt, *J* 15.5, 5.6, CH_2-C*H*=), 5.58 (1H, dd, *J* 15.5, 6.4, =C*H*CHMe), 5.76 (1H, ddd, *J* 17.2, 10.4, 6.8, C*H*=CH_2), 7.31−7.38 (5H, m, Ph). δ_C (100.6 MHz, $CDCl_3$): 19.6, 39.9, 42.9, 66.7, 113.2, 124.9, 128.1 (two peaks), 128.5, 136.6, 136.8, 142.2, 156.1. *m/z* (ES$^+$): 268 (MNa$^+$, 100%), 263 (MNH$_4^+$, 30), 255 (14), 246 (MH$^+$, 84), 241 (10), 236 (20). Accurate mass (ES$^+$): found, 246.1488; $C_{15}H_{20}NO_2$ (MH$^+$) requires 246.1494. Data for the intermediate thiocarbonate, *(4*S*,5*S*,1′*R*)-5-[(benzyloxycarbonyl)amino]methyl-4-(1-methylprop-2-enyl)-1,3-dioxolane-2-thione*, a colorless oil, are as follows. R_f 0.58 (ether). $[\alpha]^{22}_D$ +22.0° (*c* 1.17, chloroform). ν_{max}/cm^{-1} (thin film): 3412s, 2968m, 1705s, 1623m, 1455w, 1292s, 1164m, 1045w, 975w, 738w, 697m. δ_H (400 MHz, $CDCl_3$): 1.18 (3H, d, *J* 6.8, CH_3), 2.54−2.65 (1H, m, C*H*Me), 3.52−3.56 (2H, m, NHCH_2), 4.49 (1H, t, *J* 7.0, C*H*(OR)CHMe), 4.66 (1H, dt, *J* 7.0, 4.0, CH_2C*H*OR), 5.10 and 5.16 (2 × 1H, 2 × d, *J* 12.2, CH_2Ph), 5.20−5.29 (3H, m, CH=CH_2 and NH), 5.66 (1H, ddd, *J* 17.6, 9.6, 8.0, C*H*=CH_2), 7.32−7.41 (5H, m, Ph). δ_C (100.6 MHz, $CDCl_3$): 15.5, 41.4, 42.7, 67.4, 83.5, 86.4, 119.2, 128.1, 128.4, 128.6, 135.4, 135.8, 153.1, 156.7. *m/z* (ES$^+$): 344 (MNa$^+$, 12%), 322 (MH$^+$, 100), 301 (13), 195 (11). Accurate mass (ES$^+$): found, 322.1112; $C_{16}H_{20}NO_4S$ (MH$^+$) requires 322.1113.

(4*S*)-1-(Benzyloxycarbonyl)amino-4-methylhex-2(*E*),5-diene (24). With the use of the general procedure, *diene* **24** was obtained as a colorless oil (82% from diol **20**). R_f 0.62 (1:1 petrol/ether). $[\alpha]^{22}_D$ +6.22° (*c* 0.37, chloroform). ν_{max}/cm^{-1} (thin film): 3420s, 3094m, 3028m, 2963m, 2920w, 1695s, 1638m, 1529m, 1454w, 1247s, 1132w, 1045w, 970w, 912w. δ_H (500 MHz, $CDCl_3$): 1.09 (3H, d, *J* 6.5, CH_3), 2.86 (1H, app. sextet, app. *J* 6.5, C*H*Me), 3.80 (2H, br t, *J* 5.5, NHCH_2), 4.78 (1H, br s, NH), 4.97 (1H, dt, *J* 10.0, 1.5) and 5.00 (1H, dt, *J* 17.0, 1.5, CH=CH_2), 5.12 (2H, s, CH_2Ph), 5.46 (1H, dt, *J* 15.5, 5.5, CH_2C*H*=), 5.59 (1H, dd, *J* 15.5, 6.5, =C*H*CHMe), 5.76 (1H, ddd, *J* 17.0, 10.0, 6.5, C*H*=CH_2), 7.30−7.39 (5H, m, Ph). δ_C (125.7 MHz, $CDCl_3$): 19.5, 39.8, 42.8, 66.6, 113.1, 124.8, 128.0, 128.4 (two peaks), 136.4, 136.6, 142.1, 156.1. *m/z* (ES$^+$): 268 (MNa$^+$, 100%), 246 (MH$^+$, 13), 152 (8). Accurate mass (ES$^+$): found, 246.1493; $C_{15}H_{20}NO_2$ (MH$^+$) requires 246.1494. Data for the intermediate thiocarbonate, *(4*S*,5*S*,1′*S*)-5-[(benzyloxycarbonyl)amino]methyl-4-(1-methylprop-2-enyl)-1,3-dioxolane-2-thione*, a colorless oil, are as follows. R_f 0.54 (ether). $[\alpha]^{22}_D$ +10.3° (*c* 1.31, chloroform). ν_{max}/cm^{-1} (thin film): 3326m, 3066w, 3033w, 2969m, 1801w, 1710s, 1521m, 1455w, 1336s, 1290s, 1170m, 1045m, 999m, 928m, 735m, 698m. δ_H (400 MHz, $CDCl_3$): 1.16 (3H, d, *J* 6.8, CH_3), 2.60−2.70 (1H, m, C*H*Me), 3.51−3.57 (2H, m, NHCH_2), 4.64 (1H, dd, *J* 6.8, 4.4, C*H*(OR)-CHMe), 4.67 (1H, td, *J* 6.0, 4.4, CH_2C*H*O), 5.10 and 5.15 (2 × 1H, 2 × d, *J* 12.2, CH_2Ph), 5.19−5.28 (3H, m, CH=CH_2 and NH), 5.71 (1H, ddd, *J* 17.6, 10.4, 7.6, C*H*=CH_2), 7.31−7.43 (5H, m, Ph). δ_C (100.6 MHz, $CDCl_3$): 14.6, 40.2, 42.7, 67.4, 82.7, 86.6, 119.0, 128.1, 128.4, 128.6, 135.1, 135.8, 154.1, 156.8. *m/z* (APCI$^+$): 322 (MH$^+$, 48%), 236 (27), 182 (44), 171 (51), 153 (100). Accurate mass (ES$^+$): found, 322.1109; $C_{16}H_{20}NO_4S$ (MH$^+$) requires 322.1113.

(4*R*)-1-(Benzyloxycarbonyl)amino-4-methylhex-2(*Z*),5-diene (25). With the use of the general procedure, *diene* **25** was obtained as a colorless oil (48% from diol **21**). R_f 0.60 (1:1 petrol/ether). $[\alpha]^{22}_D$ +51.9° (*c* 0.27, chloroform). ν_{max}/cm^{-1} (thin film): 3335m, 3066w, 3014w, 2963m, 2927m, 1702s, 1524m, 1455w, 1260s, 1096m, 1028m, 914w, 799m, 697m. δ_H (500 MHz, $CDCl_3$): 1.09 (3H, d, *J* 6.5, CH_3), 3.15−3.26 (1H, m, C*H*Me), 3.83 and 3.90 (2 × 1H, 2 × dt, *J* 15.0, 5.0, NHC*H*$_2$), 4.72 (1H, br s, N*H*), 4.95 (1H, dt, *J* 10.5, 1.0) and 5.00 (1H, d, *J* 17.0, CH=C*H*$_2$), 5.12 (2H, s, C*H*$_2$Ph), 5.38−5.46 (2H, m, CH=CH), 5.76 (1H, ddd, *J* 17.0, 10.5, 6.5, C*H*=CH$_2$), 7.31−7.37 (5H, m, Ph). δ_C (125.7 MHz, $CDCl_3$): 20.5, 35.7, 38.1, 66.6, 112.9, 124.7, 128.0, 128.4 (two peaks), 136.4, 136.7, 142.1, 156.1. *m/z* (ES$^+$): 268 (MNa$^+$, 100%), 155 (16). Accurate mass (ES$^+$): found, 268.1314; $C_{15}H_{19}NO_2Na$ (MNa$^+$) requires 268.1313. Data for the intermediate thiocarbonate, *(4*R,5S,*1′*R*)-5-[(benzyloxycarbonyl)amino]methyl-4-(1-methylprop-2-enyl)-1,3-dioxolane-2-thione*, a colorless oil, are as follows. R_f 0.58 (ether). $[\alpha]^{22}_D$ −101.8° (*c* 0.57, chloroform). ν_{max}/cm^{-1} (thin film): 3124s, 2965m, 1701s, 1519m, 1451w, 1298s, 1160m, 975m. δ_H (400 MHz, $CDCl_3$): 1.20 (3H, d, *J* 7.2, CH_3), 2.58−2.69 (1H, m, C*H*Me), 3.39 (1H, ddd, *J* 14.8, 9.6, 4.4) and 3.85 (1H, ddd, *J* 14.8, 8.2, 2.6, NHC*H*$_2$), 4.71 (1H, t, *J* 7.4, C*H*(OR)CHMe), 4.97 (1H, ddd, *J* 9.6, 7.4, 2.6, CH$_2$C*H*O), 5.11 and 5.14 (2 × 1H, 2 × d, *J* 12.4, C*H*$_2$Ph), 5.19−5.26 (3H, m, CH=C*H*$_2$ and NH), 5.82 (1H, ddd, *J* 17.6, 10.4, 7.6, C*H*=CH$_2$), 7.32−7.41 (5H, m, Ph). δ_C (100.6 MHz, $CDCl_3$): 17.4, 37.1, 39.6, 67.3, 82.8, 86.5, 118.0, 128.1, 128.3, 128.6, 136.6, 136.7, 154.5, 157.1. *m/z* (ES$^+$): 322 (MH$^+$, 74%), 304 (19), 183 (41), 154 (100). Accurate mass (ES$^+$): found, 322.1115; $C_{16}H_{20}NO_4S$ (MH$^+$) requires 322.1113.

(3*S*,4*S*)-1-*N*-Acetyl-3,4-diacetoxy-5,5-dimethylpiperidine (28). A stirred solution of aminodiol **16** (470 mg, 1.60 mmol) and Sudan red 7B indicator (10.0 μL, 0.05% w/v in dichloromethane) in anhydrous dichloromethane (32.0 mL) was cooled to −45 °C. Ozone was passed through the solution until the magenta color dispersed; excess ozone was purged from the system with argon. Triphenylphosphine resin (3.0 mmol/g, 600 mg, 2.00 mmol) was added, and the reaction mixture was stirred at −45 °C for 30 min and then warmed to RT over 1.5 h. The resin was removed by filtration through a short plug of silica gel and Celite, and the solvents were removed from the filtrate in vacuo. The crude product was dissolved in absolute ethanol (15.0 mL), palladium on carbon (10 wt %, 55.0 mg, 0.05 mmol) was added, and the flask was purged with argon and then with hydrogen. The reaction mixture was stirred vigorously at RT under a positive pressure of hydrogen for 12 h. The flask was purged with argon and the mixture filtered through Celite to remove the palladium catalyst; the residue was washed with ethanol (3 × 5 mL), and the filtrate was concentrated in vacuo. The residual yellow foam was taken up in anhydrous dichloromethane (5.0 mL), and the solution was cooled to 0 °C; pyridine (650 μL, 8.04 mmol), DMAP (5 mg, 0.04 mmol), and acetic anhydride (1.5 mL, 16.0 mmol) were added, and the reaction mixture was warmed to RT. After 3.5 h the solution was cooled to 0 °C, and the reaction was quenched by the dropwise addition of saturated aqueous $NaHCO_3$ solution (20 mL). The mixture was partitioned between water (25 mL) and ether (25 mL); the aqueous layer was separated and extracted with ether (3 × 25 mL). The combined organic fractions were washed with brine (50 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The residual oil was azeotroped with toluene (2 × 15 mL) to remove traces of pyridine, and the crude product was purified by flash column chromatography (silica gel, ethyl acetate) to furnish the *title compound* (**28**) as a colorless syrup (77 mg, 18%). R_f 0.29 (ethyl acetate). $[\alpha]^{22}_D$ +8.62° (*c* 0.55, chloroform). ν_{max}/cm^{-1} (thin film): 2965m, 1743s, 1653s, 1439m, 1395w, 1370m, 1294w, 1242s, 1044s, 940w, 904w, 880w, 799m. δ_H (500 MHz, DMSO-d_6) [the spectrum indicates a 60:40 ratio of amide rotamers; asterisks denote resonances attributable to the minor rotamer]: 0.83,* 0.86,* 0.89 and 0.92 (6H, 4 × s, CMe$_2$), 1.97, 1.99, 2.02 and 2.05 (9H, 4 × s, 2 × OAc and NAc), 2.66 (0.6H, dd, *J* 12.5, 10.5, H-2$_{ax}$), 2.70* (0.4H, d, *J* 13.5, H-6$_{ax}$), 3.12 (0.6H, d, *J* 13.5, H-6$_{ax}$), 3.14* (1H, dd, *J* 13.5, 10.0, H-2$_{ax}$), 3.52 (0.6H, dd, *J* 13.5, 2.0, H-6$_{eq}$), 3.95* (0.4H, ddd, *J* 13.5, 5.0, 2.0, H-2$_{eq}$), 3.98* (0.4H, dd, *J* 13.5, 2.0, H-6$_{eq}$), 4.52 (0.6H, ddd, *J* 12.5, 5.5, 2.0, H-2$_{eq}$), 4.65 (0.6H, ddd, *J* 10.5, 9.5, 5.5, H-3), 4.78* (0.4H, ddd, *J* 10.0, 9.0, 5.0, H-3), 4.84* (0.4H, d, *J* 9.0, H-4), 4.85 (0.6H, d, *J* 9.5, H-4). δ_C (125.7 MHz, DMSO-d_6) [asterisks denote resonances attributable to the minor rotamer where such assignment could be made]: 19.1, 19.8, 21.4, 21.5, 21.9, 22.1, 24.5, 24.8, 37.1, 37.7, 43.2, 48.2,* 50.8,* 55.5, 68.3, 68.9,* 77.5 (two peaks), 169.4, 169.6, 170.5 (two peaks), 170.8. *m/z* (APCI$^+$): 272 (MH$^+$, 100%), 230 (10), 212 (11). Accurate mass (ES$^+$): found, 272.1497; $C_{13}H_{22}NO_5$ (MH$^+$) requires 272.1498.

(3*S*,4*S*)-1-*N*-Acetyl-5,5-dimethyl-3,4-dihydroxypiperidine (29). [In the following procedure, the Amberlite IRA 400 (OH) resin was activated by washing successively with 5% aqueous NaOH solution (6 × 3 mL) and then water until the washings were neutral. The activated resin was then washed with methanol (5 × 5 mL) before use.] To a stirred solution of acetylated piperidine **28** (74 mg, 0.27 mmol) in anhydrous methanol (5.5 mL) was added freshly activated Amberlite IRA 400 (OH) resin (2.7 mL), and the suspension was stirred vigorously at 50 °C for 12 h. The reaction mixture was cooled to RT, and the resin was removed by filtration through a glass sinter and washed with methanol (3 × 15 mL), and the filtrate was concentrated in vacuo to give *piperidine* **29** as a colorless syrup (48 mg, 94%). R_f 0.05 (ethyl acetate). ν_{max}/cm^{-1} (thin film): 3400s, 2963m, 2872m, 1624s, 1451s, 1365m, 1292w, 1251w, 1219w, 1101m, 1066m, 1042s, 1002m, 909w, 875w. δ_H (400 MHz, DMSO-d_6) [the spectrum indicates a 60:40 ratio of amide rotamers; asterisks denote resonances attributable to the minor rotamer]: 0.69,* 0.76, 0.88* and 0.94 (6H, 4 × s, CMe$_2$), 1.95 and 2.01* (3H, 2 × s, NAc), 2.23 (0.6H, dd, *J* 12.4, 10.8, H-2$_{ax}$), 2.35* (0.4H, d, *J* 12.8, H-6$_{ax}$), 2.76* (0.4H, dd, *J* 13.2, 10.0, H-2$_{ax}$), 2.81 (0.6H, d, *J* 13.2, H-6$_{ax}$), 2.91 (0.6H, d, *J* 9.0, H-4), 2.93* (0.4H, d, *J* 8.4, H-4), 3.18 (0.6H, ddd, *J* 10.8, 9.0, 5.6, H-3), 3.33* (0.4H, ddd, *J* 10.0, 8.4, 5.2, H-3), 3.39 (0.6H, dd, *J* 13.2, 2.4, H-6$_{eq}$), 3.73* (0.4H, ddd, *J* 13.2, 5.2, 2.4, H-2$_{eq}$), 3.94* (0.4H, dd, *J* 12.8, 2.4, H-6$_{eq}$), 4.40 (0.6H, ddd, *J* 12.4, 5.6, 2.4, H-2$_{eq}$), 4.80 and 4.90 (2H, 2 × br s, 2 × O*H*). δ_C (100.6 MHz, DMSO-d_6) [asterisks denote resonances attributable to the minor rotamer where such assignment could be made]: 18.5, 19.2, 22.0, 22.1, 25.6, 25.8, 37.2, 37.9, 47.2, 51.7,* 51.9,* 56.7, 68.0, 68.7,* 80.1, 80.2, 169.0. *m/z* (ES$^+$): 188 (MH$^+$, 100%), 160 (18). Accurate mass (ES$^+$): found, 188.1293; $C_9H_{18}NO_3$ (MH$^+$) requires 188.1287.

(2*S*,3*S*)-1-(Benzyloxycarbonyl)amino-2,3-diacetoxy-4,4-dimethylhex-5-ene (30). To a stirred solution of aminodiol **16** (320 mg, 1.10 mmol) in anhydrous dichloromethane (11.0 mL) cooled to 0 °C was added pyridine (222 μL, 2.75 mmol) and acetic anhydride (520 μL, 5.51 mmol), and the reaction mixture was warmed slowly to RT. After 16 h the solution was cooled to 0 °C, and the reaction was quenched by the dropwise addition of saturated aqueous $NaHCO_3$ solution (20 mL). The mixture was partitioned between water (50 mL) and ether (50 mL); the aqueous layer was separated and extracted with ether (3 × 25 mL). The combined organic fractions were washed with brine (50 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The residual oil was azeotroped with toluene (2 × 25 mL) to remove traces of pyridine, and the crude product was purified by flash column chromatography (silica gel, 1:1 petrol/ether) to furnish the *diacetate* **30** as a colorless oil (401 mg, 97%). R_f 0.63 (ether). $[\alpha]^{20}_D$ −26.4° (*c* 3.06, chloroform). ν_{max}/cm^{-1} (thin film): 3359m, 3066w, 3034w, 2972s, 1743s, 1638w, 1527m, 1456w, 1418w, 1373m, 1223s, 1148w, 1112w, 1035m, 971w, 915w, 776w, 737w, 698w. δ_H (400 MHz, $CDCl_3$): 1.00 and 1.06 (2 × 3H, 2 × s, CMe$_2$), 1.98 and 2.16 (2 × 3H, 2 × s, 2 × OAc), 3.08 (1H, dt, *J* 14.4, 5.6) and 3.35 (1H, dt, J 14.4, 7.2, NHCH_2), 4.85 (1H, d, J 2.0, CH(OAc)CMe$_2$), 4.97 (1H, d, J 17.6) and 4.99 (1H, d, J 10.8, CH=CH_2), 5.07 and 5.11 (2 × 1H, 2 × d, J 12.4, CH_2Ph), 5.13 (1H, br t, J 5.6, NH), 5.26 (1H, ddd, J 7.2, 5.6, 2.0, CH$_2$CH(OAc)), 5.91 (1H, dd, J 17.6, 10.8, CH=CH$_2$), 7.27−7.37 (5H, m, Ph). δ_C (100.6 MHz, CDCl$_3$): 20.7, 21.0, 23.1, 24.7, 40.2, 42.4, 66.8, 69.4, 77.1, 112.1, 128.1, 128.2, 128.5, 136.5, 143.3, 156.2, 170.1, 171.2. *m/z* (ES$^+$): 400 (MNa$^+$, 100%), 395 (MNH$_4^+$, 27), 378 (MH$^+$, 47), 334 (23). Accurate mass (ES$^+$): found, 400.1734; $C_{20}H_{27}NO_6Na$ (MNa$^+$) requires 400.1736.

(3*S*,4*S*,6*RS*)-1-*N*-(Benzyloxycarbonyl)-3,4-diacetoxy-5,5-dimethyl-6-hydroxypiperidine (31) and (32). A stirred solution of diacetate **30** (400 mg, 1.06 mmol) in anhydrous dichloromethane and methanol (5:1 v/v, 24.0 mL) was cooled to −45 °C. Ozone was passed through the solution until a blue coloration persisted; excess ozone was purged from the system with argon. Triphenylphosphine (695 mg, 2.65 mmol) was added, and the reaction mixture was stirred at −45 °C for 1 h and then warmed to RT. After 4.5 h the solvents were removed in vacuo, and the crude hemiaminal was purified by flash column chromatography (silica gel, 1:1 petrol/ether) to furnish the major diastereomer (**31**) as a colorless foam (243 mg, 60%) and the minor diastereomer (**32**) as a colorless syrup (120 mg, 30%). Data for **31** are as follows. R_f 0.52 (ether). $[\alpha]^{22}_D$ +8.24° (c 2.15, chloroform). ν_{max}/cm^{-1} (thin film): 3443m, 3033w, 2970m, 2007m, 1746s, 1709s, 1498w, 1429m, 1370m, 1326m, 1227s, 1168w, 1130m, 1106w, 1040s, 993w, 969w, 921w, 897w, 846w, 815w, 755w, 699w, 646w, 600m. δ_H (400 MHz, CDCl$_3$): 0.98 and 1.04 (2 × 3H, 2 × s, CMe$_2$), 2.01 and 2.06 (2 × 3H, 2 × s, 2 × OAc), 3.19 (1H, dd, J 12.0, 10.0, H-2$_{ax}$), 4.15−4.30 (1H, m, H-2$_{eq}$), 5.02 (1H, td, J 10.0, 6.4, H-3), 5.10 and 5.15 (2 × 1H, 2 × d, J 12.0, CH_2Ph), 5.35 (1H, d, J 10.0, H-4), 5.40 (1H, br s, H-6), 7.31−7.39 (5H, m, Ph). δ_C (100.6 MHz, CDCl$_3$): 19.3, 20.8, 20.9, 23.1, 40.4 (two peaks), 67.8, 68.2, 73.9, 83.0, 128.0, 128.3, 128.6, 135.9, 156.3, 170.4, 170.5. *m/z* (ES$^+$): 402 (MNa$^+$, 100%), 397 (MNH$_4^+$, 26), 362 (72), 318 (24). Accurate mass (ES$^+$): found, 402.1530; $C_{19}H_{25}NO_7Na$ (MNa$^+$) requires 402.1529. Data for **32** are as follows. R_f 0.45 (ether). $[\alpha]^{22}_D$ +1.87° (c 2.68, chloroform). ν_{max}/cm^{-1} (thin film): 3450m, 3033w, 2963m, 1745s, 1704s, 1498w, 1429m, 1372m, 1329m, 1244s, 1188m, 1164m, 1121m, 1036s, 1001m, 966w, 933w, 913w, 834w, 739w, 699m, 603m. δ_H (400 MHz, CDCl$_3$): 1.05 and 1.11 (2 × 3H, 2 × s, CMe$_2$), 1.95 and 2.12 (2 × 3H, 2 × s, 2 × OAc), 3.59 and 4.02 (2 × 1H, 2 × br d, J 14.6, H-2$_{ax}$ and H-2$_{eq}$), 4.78−4.83 (1H, m, H-3) overlays 4.82 (1H, s, H-6), 5.12 and 5.21 (2 × 1H, 2 × d, J 12.0, CH_2Ph), 5.34 (1H, d, J 6.8, H-4), 7.30−7.38 (5H, m, Ph). δ_C (100.6 MHz, CDCl$_3$): 20.9 (two peaks), 24.4 (two peaks), 37.9, 40.7, 67.4, 68.3, 74.0, 82.2, 127.9, 128.2, 128.6, 136.2, 155.7, 169.3, 169.5. *m/z* (ES$^+$): 402 (MNa$^+$, 100%), 397 (MNH$_4^+$, 11), 362 (62), 318 (30). Accurate mass (ES$^+$): found, 402.1522; $C_{19}H_{25}NO_7Na$ (MNa$^+$) requires 402.1529.

(3*S*,4*S*)-3,4-Diacetoxy-5,5-dimethylpiperidine (33). To a stirred solution of hemiaminals **31** and **32** (188 mg, 0.50 mmol) in absolute ethanol (5.0 mL) was added palladium on carbon (10 wt %, 26 mg, 0.025 mmol), and the flask was purged with argon and then with hydrogen. The reaction mixture was stirred vigorously at RT under a positive pressure of hydrogen for 16 h. The flask was purged with argon, and the mixture was filtered through Celite to remove the palladium catalyst; the residue was washed with ethanol (3 × 10 mL), and the filtrate was concentrated in vacuo to give the crude product as a white solid. Recrystallization from chloroform/ether furnished *piperidine* **33** as colorless needles (68 mg, 60%). R_f 0.11 (ethyl acetate). M.p. 189−190 °C (from chloroform/ether). $[\alpha]^{22}_D$ +14.5° (c 0.62, chloroform). ν_{max}/cm^{-1} (KBr disk): 3465m, 3065m, 2982m, 2889m, 2822w, 2786m, 2746, 2698m, 2659m, 2565w, 2511w, 2438w, 1743s, 1568w, 1462w, 1430w, 1373m, 1289w, 1236s, 1192w, 1135w, 1101w, 1050m, 1024w, 1011w, 949w, 935w, 893w, 869w, 642w, 603w, 594w. δ_H (400 MHz, CDCl$_3$): 1.13 and 1.23 (2 × 3H, 2 × s, CMe$_2$), 2.11 and 2.14 (2 × 3H, 2 × s, 2 × OAc), 2.94 and 3.04 (2 × 1H, 2 × d, J 13.0, H-6$_{ax}$ and H-6$_{eq}$), 3.18 (1H, dd, J 13.6, 6.0, H-2$_{ax}$), 3.44 (1H, dd, J 13.6, 3.6, H-2$_{eq}$), 4.87 (1H, d, J 6.0, H-4), 5.05 (1H, td, J 6.0, 3.6, H-3), 9.99 (1H, br s, NH). δ_C (100.6 MHz, CDCl$_3$): 20.6, 21.0, 22.3, 24.3, 33.9, 43.3, 50.9, 65.6, 72.9, 169.5 (two peaks). *m/z* (ES$^+$): 230 (MH$^+$, 100%). Accurate mass (ES$^+$): found, 230.1393; $C_{11}H_{20}NO_4$ (MH$^+$) requires 230.1392.

(3*S*,4*S*)-5,5-Dimethyl-3,4-dihydroxypiperidine (27). To a stirred solution of acetylated piperidine **33** (41 mg, 0.18 mmol) in anhydrous methanol (3.6 mL) was added freshly activated [see the procedure for **29**] Amberlite IRA 400 (OH) resin (1.8 mL), and the suspension was stirred vigorously at RT for 12 h. The resin was removed by filtration through a glass sinter and washed with methanol (3 × 5 mL), and the filtrate was concentrated in vacuo to give the crude product as a white solid. Recrystallization from methanol/ether furnished *piperidine* **27** as colorless needles (26 mg, 98%). R_f 0.10 (2:1 ethyl acetate/methanol). M.p. 43−45 °C (from methanol/ether). $[\alpha]^{20}_D$ +63.1° (c 0.70, methanol). ν_{max}/cm^{-1} (KBr disk): 3276s, 2927s, 2859s, 2824s, 1654w, 1541w, 1468m, 1454m, 1421m, 1362m, 1273w, 1169w, 1110m, 1082m, 1048m, 994w, 932m, 913m, 901m, 783w, 635m. δ_H (400 MHz, D$_2$O) 0.78 and 0.79 (2 × 3H, 2 × s, CMe$_2$), 2.18 (1H, dd, J 12.8, 10.8, H-2$_{ax}$), 2.24 (1H, d, J 13.2, H-6$_{ax}$), 2.44 (1H, dd, J 13.2, 1.6, H-6$_{eq}$), 2.96 (1H, ddd, J 12.8, 5.4, 1.6, H-2$_{eq}$), 3.02 (1H, d, J 9.4, H-4), 3.46 (1H, ddd, J 10.8, 9.4, 5.4, H-3). δ_C (100.6 MHz, D$_2$O) 17.8, 25.1, 36.9, 50.6, 56.3, 69.1, 80.7. *m/z* (ES$^+$): 146 (MH$^+$, 100%). Accurate mass (ES$^+$): found, 146.1187; $C_7H_{16}NO_2$ (MH$^+$) requires 146.1181.

General Procedure for Cyclohexadienyl Silane Synthesis. To a stirred solution of 1,4-cyclohexadiene (2.60 mL, 27.5 mmol) in anhydrous tetrahydrofuran (37.5 mL) cooled to −78 °C was added TMEDA (3.77 mL, 25.0 mmol) and *s*-BuLi (1.0 M in cyclohexanes, 25.0 mL, 25.0 mmol) dropwise over 10 min. The yellow solution was warmed to −45 °C and stirred for 3 h. The chlorosilane (25.0 mmol) in anhydrous tetrahydrofuran (12.5 mL) was added, and the mixture was stirred at −45 °C for a further 30 min. The solution was warmed to RT, and the reaction was quenched by the addition of saturated aqueous NH$_4$Cl solution (100 mL). The mixture was extracted with ether (3 × 50 mL), the combined organic phases were washed with brine (100 mL), dried (MgSO$_4$), and the solvent was removed in vacuo. The resulting oil was purified by flash column chromatography (silica gel, 40−60 petrol) to furnish the cyclohexadienyl silane.

(Cyclohexa-2,5-dienyl)diphenylsilane (34). Colorless oil (6.56 g, 100% from diphenylchlorosilane). R_f 0.35 (petrol). ν_{max}/cm^{-1} (thin film): 3068m, 3048m, 3025m, 2885w, 2854w, 2820m, 2125s, 1956w, 1884w, 1819w, 1667w, 1622w, 1588w, 1486w, 1428s, 1331w, 1293w, 1190w, 1158w, 1115s, 1066w, 1052w, 998w, 931w, 893m, 803s, 726s, 698s. δ_H (400 MHz, CDCl$_3$): 2.36−2.46 and 2.61−2.72 (2 × 1H, 2 × m, CH$_2$), 2.95−3.03 (1H, m, SiCH), 4.83 (1H, d, J 3.2, SiH), 5.57−5.63 (2H, m) and 5.76−5.82 (2H, m, 2 × CH=CH), 7.37−7.47 (6H, m) and 7.64−7.68 (4H, m, 2 × Ph). δ_C (100.6 MHz, CDCl$_3$): 26.2, 28.4, 123.2, 125.2, 127.9, 129.7, 132.9, 135.5. *m/z* (CI$^+$): 280 (MNH$_4^+$, 38%), 263 (MH$^+$, 53), 200 (100), 183 (58), 139 (12), 123 (39), 105 (19). Accurate mass (CI$^+$): found, 280.1511; $C_{18}H_{22}NSi$ (MNH$_4^+$) requires 280.1522.

(Cyclohexa-2,5-dienyl)di(isopropyl)silane (35). Colorless oil (4.69 g, 96% from di(isopropyl)chlorosilane). R_f 0.61 (petrol). ν_{max}/cm^{-1} (thin film): 3025m, 2941s, 2890s, 2864s, 2821m, 2093s, 1624w, 1462m, 1384w, 1366w, 1291w, 1244w, 1108m, 1053w, 1004m, 897m, 883m, 824m, 801s, 732s, 653m, 625m. δ_H (400 MHz, CDCl$_3$): 1.08−1.11 (14H, m, 2 × *i*-Pr), 2.54−2.62 (1H, m, SiCH), 2.70−2.78 (2H, m, CH$_2$), 3.45 (1H, d, J 1.7, SiH), 5.52−5.58 (2H, m), and 5.70−5.76 (2H, m, 2 × CH=CH). δ_C (100.6 MHz, CDCl$_3$): 10.4, 19.1, 19.2, 26.1, 26.4, 121.6, 126.6. *m/z* (CI$^+$): 212 (MNH$_4^+$, 72%), 195 (MH$^+$, 100), 147 (20), 132 (51), 130 (34), 104 (13), 90 (45), 76 (15). Accurate mass (CI$^+$): found, 195.1564; $C_{12}H_{23}Si$ (MH$^+$) requires 195.1569.

Ethyl [(cyclohexa-2,5-dienyl)diphenylsilanyloxy]phenylacetate (37). A flame-dried two-necked flask (50 mL) was charged with anhydrous CuCl$_2$ (0.51 g, 3.82 mmol) and anhydrous CuI (10 mg, 0.05 mmol). The flask was equipped with a flame-dried Schlenk filter attached to a second round-bottomed flask (50 mL). All joints were sealed with PTFE tape, and the apparatus was purged several times with argon. Anhydrous tetrahydrofuran (10.0 mL) was added followed by the cyclohexadienylsilane **34** (0.5 g, 1.91 mmol), and the orange suspension was stirred for 27 h at RT. The apparatus was inverted, and the inorganics were filtered off by suction under argon. The solution of crude chlorosilane (**36**) in tetrahydrofuran was added via cannula to a stirred solution of (±)-ethyl mandelate (0.31 mL, 1.90 mmol), DMAP (6 mg, 0.05 mmol), and triethylamine (0.8 mL, 5.70 mmol) in anhydrous DMF (38 mL). The reaction mixture was warmed to 40 °C for 5 h, then cooled to RT and partitioned between water (100 mL) and ether (25 mL). The aqueous phase was extracted with ether (3 × 50 mL), and the combined organic fractions were washed with brine (100 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The resulting yellow oil was purified by flash column chromatography (silica gel, 20:1 petrol/ether) to furnish the *title compound* (**37**) as a colorless oil (737 mg, 88%). R_f 0.53 (2:1 petrol/ether). ν_{max}/cm^{-1} (thin film): 3069w, 3028m, 3000w, 2980w, 2936w, 2889w, 2856w, 2821w, 1960w, 1892w, 1824w, 1752s, 1590w, 1494w, 1454w, 1429m, 1264m, 1206m, 1178m, 1120s, 1072m, 1028m, 948w, 892m, 836m. δ_H (400 MHz, $CDCl_3$): 1.11 (3H, t, *J* 7.2, CH_3), 2.06−2.17 and 2.50−2.61 (2 × 1H, 2 × m, CH_2), 3.12−3.19 (1H, m, SiCH), 4.00 (2H, 2 × dq, *J* 10.8, 7.2, OCH_2), 5.29 (1H, s, OC*H*Ph), 5.50−5.55 (2H, m) and 5.78−5.86 (2H, m, 2 × CH═CH), 7.30−7.74 (15H, m, 3 × Ph). δ_C (100.6 MHz, $CDCl_3$): 13.9, 26.0, 30.1, 61.0, 74.8, 123.5, 123.6, 124.2, 124.3, 126.6−135.5 (series of overlapping peaks), 132.5, 132.6, 138.7, 171.6. *m/z* (CI$^+$): 458 (MNH_4^+, 17%), 361 (100), 207 (13), 199 (22), 182 (55). Accurate mass (CI$^+$): found, 361.1257; $C_{22}H_{21}O_3Si$ ($M^+-C_6H_7$) requires 361.1260.

[(Cyclohexa-2,5-dienyl)diphenylsilanyloxy]phenylacetaldehyde (38). To a stirred solution of ester **37** (220 mg, 0.5 mmol) in anhydrous dichloromethane (5.0 mL), cooled to −78 °C, was added DIBAL (0.75 mL, 1.0 M in dichloromethane, 0.75 mmol) dropwise, and the solution was stirred at −78 °C for 45 min. The reaction was quenched by the addition of a saturated solution of tartaric acid in methanol (2 mL). The mixture was warmed to RT and partitioned between aqueous tartaric acid solution (30% w/v, 25 mL) and ether (25 mL). The aqueous layer was extracted with ether (3 × 25 mL), and the combined organic extracts were washed with brine (50 mL), dried (Na_2SO_4), and the solvents were removed in vacuo. The crude product was purified by flash column chromatography (silica gel, 20:1 petrol/ether) to furnish the *aldehyde* (**38**) as a colorless oil (61 mg, 31%). [Aldehyde **38** is unstable toward chromatography and was generally used crude.] R_f 0.49 (2:1 petrol/ether [streaks]). ν_{max}/cm^{-1} (thin film): 3069m, 3049w, 3028m, 2955w, 2924w, 2889w, 2854w, 2820w, 1960w, 1891w, 1825w, 1736s, 1590w, 1489w, 1453w, 1429s, 1191m, 1118s, 1073m, 1051m, 1028m, 924w, 895w, 853w, 741m, 711s, 699s. δ_H (400 MHz, $CDCl_3$): 2.10−2.21 and 2.55−2.65 (2 × 1H, 2 × m, CH_2), 3.14−3.22 (1H, m, SiCH), 5.20 (1H, d, *J* 1.6, C*H*Ph), 5.53−5.60 and 5.78−5.86 (2 × 2H, 2 × m, 2 × CH═CH), 7.30−7.75 (15H, m, 3 × Ph), 9.59 (1H, d, *J* 1.6, C*H*O). δ_C (100.6 MHz, $CDCl_3$): 26.1, 30.0, 80.6, 123.4, 123.5, 124.2, 124.4, 126.5−136.0 (series of overlapping peaks), 132.4 (two peaks), 136.1, 198.9. *m/z* (CI$^+$): 397 (MH$^+$, 20%), 224 (100), 197 (47), 180 (33), 163 (14). Accurate mass (CI$^+$): found, 397.1602; $C_{26}H_{25}O_2Si$ (MH$^+$) requires 397.1624.

(1*S,2*S**,1′*S**)-1-(Cyclohexa-2,4-dienyl)-2-phenylethan-1,2-diol (40).** A degassed solution of crude aldehyde **38** (assumed 0.5 mmol) in anhydrous toluene (5.0 mL) was heated at 120 °C in a base-washed sealed tube. After 20 h the reaction mixture was cooled to RT and the solvent was removed in vacuo. The crude dioxasilolane (**39**) was dissolved in methanol (5.0 mL). KF (90 mg, 1.55 mmol) and H_2O_2 (35% in water, 500 μL) were added, and the reaction mixture was stirred at RT for 2 h. The solvent was removed in vacuo, and the residue was taken up in ether (25 mL) and washed with water (25 mL). The aqueous phase was extracted with ether (2 × 15 mL), and the combined organic fractions were washed with brine (50 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The residual oil was purified by flash column chromatography (silica gel, 5:1 petrol/ether) to furnish the *title compound* (**40**) (21 mg, 19% from ester **37**) and a diastereomer, tentatively assigned as the (1*R**,2*S**,1′*R**)-isomer **41** (7 mg, 6% from ester **37**), both as colorless crystalline solids. Data for **40** are as follows. R_f 0.54 (ether). M.p. 100−103 °C (chloroform). ν_{max}/cm^{-1} (KBr disk): 3392s, 3036m, 2921w, 1951w, 1891w, 1818w, 1691w, 1600w, 1494w, 1452w, 1429w, 1409w, 1198w, 1116m, 1064m, 1026m, 971w, 919w, 842w, 761m, 700s. δ_H (500 MHz, $CDCl_3$): 2.24−2.29 (2H, m, CH_2), 2.31 (1H, d, *J* 5.0, CH(O*H*)CH), 2.43 (1H, dddd, *J* 10.5, 4.5, 4.0, 2.5, CH(OH)C*H*), 2.78 (1H, d, *J* 3.9, CH(O*H*)Ph), 3.64 (1H, dt, *J* 10.5, 5.0, C*H*(OH)CH), 4.73 (1H, dd, *J* 5.0, 3.9, C*H*(OH)-Ph), 5.81 (1H, dt, *J* 9.5, 4.5, ═C*H*CH_2), 5.86 (1H, dd, *J* 9.5, 4.5, C*H*═CHCH_2), 5.87−5.91 (1H, m) and 6.06 (1H, dd, *J* 9.5, 4.5, CHC*H*═C*H*), 7.29−7.40 (5H, m, Ph). δ_C (125.7 MHz, $CDCl_3$): 26.5, 34.5, 74.2, 79.1, 123.7, 125.0, 126.2, 126.3, 126.5, 127.9, 128.5, 141.0. *m/z* (CI$^+$): 234 (MNH_4^+, 100%), 217 (MH$^+$, 18), 199 (22), 154 (12), 137 (16), 121 (30), 105 (15), 91 (17). Accurate mass (CI$^+$): found, 234.1493; $C_{14}H_{20}NO_2$ (MNH_4^+) requires 234.1494. Data for **41** are as follows. R_f 0.58 (ether). M.p. 75−77 °C (from chloroform). ν_{max}/cm^{-1} (KBr disk): 3428s, 3015s, 2925m, 2873m, 1954w, 1885w, 1813w, 1719w, 1604w, 1494m, 1454m, 1429m, 1410m, 1392m, 1216s, 1078m, 1060m, 1023s, 973w, 924w, 843w, 755s, 702s. δ_H (500 MHz, $CDCl_3$): 1.97 (1H, d, *J* 5.0, CH(O*H*)CH), 2.24−2.33 (3H, m, CH_2 and CH(O*H*)Ph), 2.54−2.61 (1H, m, CH(OH)C*H*), 3.80 (1H, dt, *J* 9.5, 5.0, C*H*(OH)CH), 4.79 (1H, d, *J* 5.0, C*H*(OH)Ph), 5.80 (1H, dt, *J* 9.5, 4.0, ═C*H*CH_2), 5.87−5.90 (1H, m, C*H*═CH), 5.91 (1H, dd, *J* 9.5, 4.0, C*H*═CHCH_2), 6.03 (1H, dd, *J* 9.5, 5.0, CH═C*H*), 7.31−7.44 (5H, m, Ph). δ_C (125.7 MHz, $CDCl_3$): 26.4, 34.3, 75.1, 78.1, 123.9, 125.6, 125.7, 126.0, 126.9, 127.8, 128.4, 140.5. *m/z* (CI$^+$): 234 (MNH_4^+, 52%), 217 (MH$^+$, 40), 199 (74), 183 (24), 154 (29), 136 (43), 121 (50), 105 (100), 94 (69), 78 (73). Accurate mass (CI$^+$): found, 234.1471; $C_{14}H_{20}NO_2$ (MNH_4^+) requires 234.1494.

2-[(Cyclohexa-2,5-dienyl)diphenylsilanyloxy]-3,3-dimethylbutyronitrile (42). A flame-dried two-necked flask (50 mL) was charged with anhydrous $CuCl_2$ (1.03 g, 7.66 mmol) and anhydrous CuI (73 mg, 0.38 mmol). The flask was equipped with a flame-dried Schlenk filter attached to a second round-bottomed flask (50 mL). All joints were sealed with PTFE tape, and the apparatus was purged several times with argon. Anhydrous tetrahydrofuran (15 mL) was added, followed by the cyclohexadienylsilane (**34**) (1.0 g, 3.81 mmol), and the orange suspension was stirred for 12 h at RT. The apparatus was inverted, and the inorganics were filtered off by suction under argon. The solution of crude chlorosilane (**36**) in tetrahydrofuran was added via cannula to a stirred solution of pivalaldehyde cyanohydrin[20] (216 mg, 1.91 mmol), DMAP (584 mg, 4.78 mmol), and triethylamine (531 μL, 3.81 mmol) in anhydrous dichloromethane (20 mL). The reaction mixture was stirred at RT for 22 h, then partitioned between saturated aqueous $NaHCO_3$ solution (100 mL) and ether (50 mL). The aqueous phase was extracted with ether (3 × 50 mL), the combined organic layers were washed with brine (100 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The resulting oil was purified by flash column chromatography (silica gel, petrol → 50:1 petrol/ether) to furnish *silylcyanohydrin* **42** as a colorless oil (700 mg, 98%). R_f 0.58 (2:1 petrol/ether). ν_{max}/cm^{-1} (thin film): 3071w, 3050w, 3028m, 2966m, 2873w, 2821w, 2245w, 1961w, 1892w, 1824w, 1591w, 1477m, 1465w, 1429s, 1398w, 1368m, 1335w, 1193w, 1119s, 1035s, 1014s, 994s, 894w, 827m, 778w, 740s, 699s, 625s, 614s. δ_H (400 MHz, $CDCl_3$): 1.05 (9H, s, *t*-Bu), 2.07 (1H, dtt, *J* 13.6, 5.2, 2.8) and 2.53−2.63 (1H, m, CH_2), 3.26−3.34 (1H, m, SiCH),

(20) Meerpoel, L.; Hoornaert, G. *Synthesis* **1990**, 905−908 and references therein.

4.04 (1H, s, CHCN), 5.56−5.62 and 5.83−5.93 (2 × 2H, 2 × m, 2 × CH=CH), 7.41−7.75 (10H, m, 2 × Ph). δ_C (100.6 MHz, $CDCl_3$): 25.1, 26.1, 29.6, 36.3, 71.6, 118.7, 123.8, 123.9 (two peaks), 124.2, 127.9, 128.1, 130.5, 130.6, 131.2, 131.3, 134.6, 135.6. *m/z* (CI^+): 391 (MNH_4^+, 100%), 374 (MH^+, 10), 311 (37), 294 (26), 267 (14), 215 (13), 198 (10). Accurate mass (CI^+): found, 294.1302; $C_{18}H_{20}NOSi$ ($M^{+}-C_6H_7$) requires 294.1314.

2-[(Cyclohexa-2,5-dienyl)diphenylsilanyloxy]-3,3-dimethylbutyraldehyde (43). To a stirred solution of silylcyanohydrin **42** (920 mg, 2.47 mmol) in anhydrous dichloromethane (25 mL) cooled to −78 °C was added DIBAL (1.0 M in dichloromethane, 3.70 mL, 3.70 mmol) dropwise, and the solution was stirred at −78 °C for 3 h and then warmed to −45 °C and stirred for a further 2 h. The reaction was quenched by the addition of a saturated solution of tartaric acid in methanol (5 mL). The mixture was warmed to RT and partitioned between aqueous tartaric acid solution (20% w/v, 50 mL) and ether (50 mL). The aqueous layer was extracted with ether (3 × 25 mL), and the combined organic extracts were washed with brine (50 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The crude product was purified by flash column chromatography (silica gel, 50:1 petrol/ether) to furnish *aldehyde* **43** as a colorless syrup (842 mg, 91%). R_f 0.60 (2:1 petrol/ether). ν_{max}/cm^{-1} (thin film): 3070w, 3028w, 2962m, 2871w, 2820w, 1734s, 1590w, 1478w, 1429s, 1396w, 1366m, 1190w, 1119s, 1035s, 1014s, 994m, 935w, 894m, 841m, 740s, 699s, 624s, 614s. δ_H (400 MHz, $CDCl_3$): 0.98 (9H, s, *t*-Bu), 2.03 (1H, dtt, *J* 13.6, 5.2, 2.8) and 2.49−2.60 (1H, m, CH_2), 3.15−3.22 (1H, m, SiCH), 3.67 (1H, d, *J* 2.6, OCH), 5.48−5.58 and 5.76−5.89 (2 × 2H, 2 × m, 2 × CH=CH), 7.35−7.77 (10H, m, 2 × Ph), 9.58 (1H, d, *J* 2.6, CHO). δ_C (100.6 MHz, $CDCl_3$): 25.9, 26.0, 29.9, 36.1, 85.1, 123.6, 123.7, 124.1, 124.2, 127.8, 127.9, 130.3, 130.4, 132.5, 134.0, 134.3, 135.6, 203.5. *m/z* (CI^+): 377 (MH^+, 49%), 315 (26), 311 (28), 297 (100), 216 (17), 198 (20), 181 (28), 179 (24), 163 (42). Accurate mass (CI^+): found, 297.1304; $C_{18}H_{21}O_2Si$ ($M^+-C_6H_7$) requires 297.1311.

(1*S,2*S**,1′*S**)-1-(Cyclohexa-2,4-dienyl)-3,3-dimethylbutan-1,2-diol (44).** A degassed solution of aldehyde **43** (842 mg, 2.24 mmol) in anhydrous toluene (12 mL) was heated at 130 °C in a base-washed sealed tube. After 18 h the reaction mixture was cooled to RT, and the solvent was removed in vacuo. The crude dioxasilolane was dissolved in tetrahydrofuran (22 mL), cooled to 0 °C, and TBAF (1.0 M in tetrahydrofuran, 5.60 mL, 5.60 mmol) was added dropwise. The reaction mixture was stirred for 30 min at 0 °C and then warmed to RT and stirred for a further 1.5 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl solution (50 mL). The mixture was extracted with ether (3 × 50 mL), and the combined organic phases were washed with brine (100 mL), dried ($MgSO_4$), and the solvent was removed in vacuo. The crude product was purified by flash column chromatography (silica gel, 10:1 petrol/ether) to furnish *diol* **44** as a colorless crystalline solid (376 mg, 86%). R_f 0.39 (1:1 petrol/ether). M.p. 86−88 °C (ether). ν_{max}/cm^{-1} (KBr disk): 3445s and 3338s, 3040m, 2957s, 2868m, 2821w, 1480w, 1428w, 1392w, 1361w, 1307w, 1102m, 1050m, 1016m, 986w, 932w, 872w, 852w, 830w, 772w, 740w, 689s. δ_H (400 MHz, $CDCl_3$): 0.93 (9H, s, *t*-Bu), 2.16 (1H, dddd, *J* 13.2, 11.2, 4.4, 2.0) and 2.31 (1H, dddd, *J* 13.2, 9.2, 4.4, 2.0, CH_2), 2.32 (1H, d, *J* 6.8, CH(O*H*)CH), 2.43−2.52 (1H, m, CH(OH)C*H*), 2.48 (1H, d, *J* 6.8, *t*-BuCH(O*H*)), 3.25 (1H, d, *J* 6.8, *t*-BuC*H*), 3.73 (1H, t, *J* 6.8, C*H*(OH)CH), 5.78 (1H, dt, *J* 9.6, 4.4, =C*H*CH_2), 5.86−5.94 (2H, m, C*H*=CHCH_2 and C*H*=CH), 6.00−6.06 (1H, m, CH=C*H*). δ_C (100.6 MHz, $CDCl_3$): 25.4, 26.0, 35.1, 38.0, 70.7, 77.2, 124.3, 125.6, 125.7, 126.9. *m/z* (CI^+): 214 (MNH_4^+, 43%), 197 (MH^+, 100), 179 (94), 163 (18), 134 (45), 126 (17), 114 (34), 109 (43), 98 (30), 94 (41), 85 (26), 78 (70), 58 (35). Accurate mass (CI^+): found, 197.1536; $C_{12}H_{21}O_2$ (MH^+) requires 197.1541.

(4*S,5*S**,1′*S**)-5-(*tert*-Butyl)-4-(cyclohexa-2,4-dienyl)-2,2-dimethyl-1,3-dioxolane (45).** To a stirred solution of diol **44** (350 mg, 1.79 mol) in 2,2-dimethoxypropane (5.0 mL) was added CSA (21 mg, 0.09 mmol), and the reaction mixture was stirred at RT for 1.5 h. The reaction mixture was partitioned between saturated aqueous $NaHCO_3$ solution (50 mL) and ether (50 mL); the aqueous phase was separated and extracted with ether (3 × 25 mL). The combined organic fractions were washed with brine (50 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The residual oil was purified by flash column chromatography (silica gel, 20:1 petrol/ether) to furnish *acetonide* **45** as a colorless oil (337 mg, 80%). R_f 0.74 (5:1 petrol/ether). ν_{max}/cm^{-1} (thin film): 3041w, 2983m, 2957m, 2871m, 1480w, 1468w, 1430w, 1395w, 1378m, 1368s, 1249s, 1208m, 1162m, 1115w, 1077m, 1053m, 1027m, 994w, 973w, 928w, 872w, 700m, 681m, 659w. δ_H (400 MHz, $CDCl_3$): 0.93 (9H, s, *t*-Bu), 1.41 (6H, s, CMe_2), 2.13−2.19 (2H, m, CH_2), 2.51−2.61 (1H, m, CH(OR)C*H*), 3.67 (1H, d, *J* 6.0, *t*-BuC*H*), 3.87 (1H, t, *J* 6.0, C*H*(OR)CH), 5.76−5.83 (1H, m), 5.91−5.96 (2H, m) and 5.98−6.04 (1H, m, 2 × CH=CH). δ_C (100.6 MHz, $CDCl_3$): 26.2, 27.1, 27.5, 28.4, 33.4, 37.8, 79.6, 86.7, 108.6, 124.7, 125.0, 125.6, 127.0. *m/z* (CI^+): 237 (MH^+, 100%), 179 (78), 157 (94), 148 (51), 126 (13). Accurate mass (CI^+): found, 237.1854; $C_{15}H_{25}O_2$ (MH^+) requires 237.1855.

(4*S,5*S**,1′*S**,4′*R**,5′*S**)-5-(*tert*-Butyl)-4-(4,5-dibenzyloxycyclohex-2-enyl)-2,2-dimethyl-1,3-dioxolane (47).** To a stirred solution of dioxolane **45** (172 mg, 0.73 mol) in tetrahydrofuran (7.0 mL) was added NMO (171 mg, 1.46 mmol) and OsO_4 (10 mg, 0.04 mmol; the mixture was stirred at RT for 3 h, then the reaction was quenched by the addition of dilute aqueous Na_2SO_3 solution (10% w/v, 10 mL). The mixture was partitioned between water (50 mL) and ethyl acetate (50 mL), and the aqueous phase was separated and extracted with ethyl acetate (3 × 25 mL). The combined organic fractions were washed with brine (100 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The residue was azeotroped with toluene (3 × 10 mL) and then dissolved in anhydrous DMF (7.0 mL), and the solution was cooled to 0 °C. Benzyl bromide (695 μL, 5.84 mmol) was added, followed by NaH (233 mg of a 60% dispersion in mineral oil, 5.83 mmol). The reaction mixture was allowed to warm slowly to RT over 16 h. The solution was cooled to 0 °C, and the reaction was quenched by the dropwise addition of methanol (2 mL); the resulting mixture was partitioned between water (50 mL) and ether (50 mL). The aqueous phase was separated and extracted with ether (2 × 50 mL); the combined organic fractions were washed with brine (100 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The residual oil was azeotroped with toluene (2 × 15 mL) to remove traces of DMF. Purification by flash column chromatography (silica gel, 10:1 petrol/ether) gave the *title compound* (**47**) as a colorless oil (107 mg, 33%). R_f 0.48 (2:1 petrol/ether). ν_{max}/cm^{-1} (thin film): 3087w, 3063w, 3030w, 2981m, 2955m, 2926m, 2870m, 1949w, 1871w, 1809w, 1725w, 1651w, 1606w, 1496w, 1479w, 1454m, 1378m, 1368m, 1332w, 1247m, 1214m, 1167w, 1114s, 1074s, 1028s, 933w, 908w, 902w, 871w, 816w, 735s, 698s. δ_H (400 MHz, $CDCl_3$): 0.94 (9H, s, *t*-Bu), 1.35 and 1.38 (2 × 3H, 2 × s, CMe_2), 1.57 (1H, ddd, *J* 13.6, 9.0, 2.0) and 2.04 (1H, ddd, *J* 13.6, 6.8, 5.4, CH_2CH), 2.61−2.68 (1H, m, CH(OR)C*H*), 3.65 (1H, d, *J* 7.0, *t*-BuC*H*), 3.70 (1H, dd, *J* 7.0, 4.4, C*H*(OR)CH), 3.00−4.05 and 4.05−4.09 (2 × 1H, 2 × m, 2 × C*H*(OBn)), 4.61 and 4.68 (2 × 1H, 2 × d, *J* 12.4, CH_2Ph), 4.66 and 4.72 (2 × 1H, 2 × d, *J* 12.6, CH_2Ph), 5.85 (1H, br d, *J* 10.6) and 5.99 (1H, br d, *J* 10.6, CH=CH), 7.27−7.42 (10H, m, 2 × Ph). δ_C (100.6 MHz, $CDCl_3$): 26.2, 27.5, 28.1, 30.0, 33.0, 36.2, 70.5, 71.4, 72.7, 74.1, 80.5, 85.9, 108.3, 127.4, 127.5, 127.6, 127.7, 127.9, 128.3 (two peaks), 129.4, 138.8, 139.0. *m/z* (ES^+): 473 (MNa^+, 89%), 468 (MNH_4^+, 100), 343 (62), 279 (20). Accurate mass (ES^+): found, 451.2856; $C_{29}H_{39}O_4$ (MH^+) requires 451.2848.

(1*S,2*S**,1′*S**,4′*R**,5′*S**)-1-(4,5-Dibenzyloxycyclohexa-2-enyl)-3,3-dimethyl butan-1,2-diol.** To a stirred solution of dioxolane **47** (80 mg, 0.18 mmol) in water (3.0 mL) was added TFA (6.0 mL), and the mixture was stirred at RT for 2 h. The solution was concentrated in vacuo employing toluene (3 × 10 mL) to remove water azeotropically. The residual yellow oil was purified by flash column chromatography (silica gel, 1:1 petrol/ether) to furnish the *title compound* as a colorless oil (72 mg, 99%). R_f 0.23 (1:1 petrol/ether). ν_{max}/cm^{-1} (thin film): 3429m, 3088w, 3064w, 3031w, 2954s, 2868m, 1951w, 1875w, 1812w, 1648w, 1606w, 1496w, 1478w, 1454m, 1395m, 1363m, 1306w, 1254w, 1206w, 1090s, 1075s, 1028m, 1014m, 957w, 910m, 855w, 805w, 735s, 698s. δ_H (400 MHz, $CDCl_3$): 0.92 (9H, s, *t*-Bu), 1.50 (1H, ddd, *J* 13.8, 8.6, 1.6) and 2.12 (1H, ddd, *J* 13.8, 7.0, 5.6, CH_2), 2.25 and 2.31 (2 × 1H, 2 × br s, 2 × OH), 2.50−2.60 (1H, m, CH(OH)C*H*), 3.17 (1H, br s, *t*-BuC*H*), 3.61 (1H, d, *J* 5.6, C*H*(OH)CH), 3.94−3.99 and 4.02−4.05 (2 × 1H, 2 × m, 2 × C*H*(OBn)), 4.59 and 4.67 (2 × 1H, 2 × d, *J* 12.4, CH_2Ph), 4.69 (2H, s, CH_2Ph), 5.85 and 5.92 (2 × 1H, 2 × br d, *J* 10.4, CH=CH), 7.26−7.43 (10H, m, 2 × Ph). δ_C (100.6 MHz, $CDCl_3$): 25.9, 27.3, 35.0, 39.0, 70.6, 71.1, 71.2, 72.4, 74.0, 77.1, 127.4, 127.5, 127.6, 127.9, 128.2, 128.3 (two peaks), 130.1, 138.7, 139.0. *m/z* (ES$^+$): 433 (MNa$^+$, 100%), 428 (MNH_4^+, 34), 303 (17), 279 (71). Accurate mass (ES$^+$): found, 428.2809; $C_{26}H_{38}NO_4$ (MNH_4^+) requires 428.2801.

(1*S,2*R**,5*S**)-1,2-Dibenzyloxy-5-(hydroxymethyl)cyclohex-3-ene (48).** To a stirred solution of (1*S**,2*S**,1′*S**,4′*R**,5′*S**)-1-(4,5-dibenzyloxycyclohexa-2-enyl)-3,3-dimethylbutan-1,2-diol (71 mg, 0.17 mmol) in tetrahydrofuran (3.0 mL) and water (1.0 mL) was added $NaIO_4$ (167 mg, 0.78 mmol). The reaction mixture was stirred vigorously at RT for 2.5 h, and then the reaction was quenched by the addition of brine (25 mL). The resulting mixture was extracted with ethyl acetate (3 × 15 mL); the combined organic fractions were dried ($MgSO_4$), and the solvents were removed in vacuo. The residue was dissolved in methanol (4.0 mL), and the resulting solution was cooled to 0 °C; $NaBH_4$ (33 mg, 0.87 mmol) was added, and the reaction mixture was stirred for 30 min. The reaction was quenched by the addition of saturated aqueous NH_4Cl solution (15 mL); the aqueous phase was extracted with ethyl acetate (3 × 15 mL), and the combined organic fractions were washed with brine (25 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The resulting pale yellow oil was purified by flash column chromatography (silica gel, 1:1 petrol/ether) to furnish the *title compound* (**48**) as a colorless oil (45 mg, 80%). R_f 0.40 (ether). ν_{max}/cm^{-1} (thin film): 3434m, 3062w, 3029w, 2923m, 2869s, 1955w, 1876w, 1817w, 1724w, 1654w, 1604w, 1496w, 1454m, 1390w, 1359w, 1336w, 1306w, 1206w, 1098s, 1071s, 1038s, 1028s, 910w, 803w, 736s, 697s. δ_H (400 MHz, $CDCl_3$): 1.54 (1H, ddd, *J* 13.6, 8.0, 2.0, C*H*H′), 1.57 (1H, br s, 6-O*H*), 2.18 (1H, dt, *J* 13.6, 6.8, CH*H*′), 2.55−2.63 (1H, m, C*H*CH$_2$), 3.55 (1H, dd, *J* 10.6, 5.4) and 3.59 (1H, dd, *J* 10.6, 6.0, CH_2-OH), 3.92−3.97 and 4.02−4.05 (2 × 1H, 2 × m, 2 × C*H*(OBn)), 4.60 and 4.67 (2 × 1H, 2 × d, *J* 12.4, CH_2Ph), 4.69 and 4.72 (2 × 1H, 2 × d, *J* 12.8, CH_2Ph), 5.79 and 5.85 (2 × 1H, 2 × br d, *J* 10.4, HC=CH), 7.26−7.43 (10H, m, 2 × Ph). δ_C (100.6 MHz, $CDCl_3$): 27.0, 36.2, 66.2, 70.7, 70.9, 72.4, 73.7, 127.4, 127.5, 127.6, 127.8, 128.0, 128.3 (two peaks), 130.8, 138.8, 138.9. *m/z* (ES$^+$): 347 (MNa$^+$, 65%), 342 (MNH_4^+, 100), 325 (MH$^+$, 14), 217 (19). Accurate mass (ES$^+$): found, 347.1626; $C_{21}H_{24}O_3Na$ (MNa$^+$) requires 347.1623.

(1*S,2*S**,3*S**,4*S**,5*R**)-1,2-Dibenzyloxy-3,4-epoxy-5-(hydroxymethyl)cyclohexane (49).** To a blue-green suspension of VO(acac)$_2$ (1.6 mg, 0.006 mmol) in anhydrous dichloromethane (1.5 mL) cooled to 0 °C was added cyclohexene derivative **48** (36 mg, 0.11 mmol) in anhydrous dichloromethane (1.0 mL). After 10 min *tert*-butylhydroperoxide (5.0 M in decane, 34.0 μL, 0.17 mmol) was added, and the dark-red solution was stirred vigorously for 1 h at 0 °C and then warmed to RT. After 6 h the reaction was quenched by the addition of dilute aqueous Na_2SO_3 solution (10% w/v, 10 mL), and the mixture was extracted with ether (3 × 15 mL). The combined organic fractions were washed with brine (25 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The residue was purified by flash column chromatography (silica gel, 2:1 petrol/ether) to furnish *epoxide* **49** as a colorless oil (20.5 mg, 54%). R_f 0.29 (ether). ν_{max}/cm^{-1} (thin film): 3436m, 3058w, 3023w, 2928m, 2870m, 1496w, 1453m, 1355w, 1325w, 1312w, 1261w, 1206w, 1112s, 1095s, 1072s, 1027m, 800w, 734m, 698s. δ_H (400 MHz, $CDCl_3$): 1.12 (1H, ddd, *J* 14.2, 10.2, 1.6) and 1.83 (1H, dt, *J* 14.2, 6.4, CHCH_2), 2.38−2.47 (1H, m, C*H*CH$_2$), 3.28 (1H, br d, *J* 3.8, CH(OBn)C*H*O), 3.38−3.42 (1H, m, C*H*(OR)CHCH$_2$), 3.62 (1H, d, *J* 3.8, C*H*(OBn)CHO), 3.71−3.76 (2H, m, CH_2OH), 3.77−3.82 (1H, m, CH$_2$C*H*(OBn)), 4.63 and 4.68 (2 × 1H, 2 × d, *J* 12.2, CH_2Ph), 4.67 and 4.71 (2 × 1H, 2 × d, *J* 12.0, CH_2Ph), 7.30−7.44 (10H, m, 2 × Ph). δ_C (100.6 MHz, $CDCl_3$): 22.8, 32.7, 53.9, 54.6, 64.9, 71.2, 71.4, 71.6, 75.1, 127.6, 127.7, 128.3, 128.4, 138.8, 138.9. *m/z* (ES$^+$): 363 (MNa$^+$, 100%), 358 (MNH_4^+, 12), 255 (13). Accurate mass (ES$^+$): found, 363.1569; $C_{21}H_{24}O_4Na$ (MNa$^+$) requires 363.1572.

(1*S,2*S**,3*R**,4*R**,5*R**)-3-Acetoxy-5-(acetoxymethyl)-1,2-dibenzyloxy-4-chlorocyclohexane (51).** To a stirred solution of epoxide **49** (6.0 mg, 0.018 mmol) in tetrahydrofuran (1.5 mL) and water (300 μL) was added hydrochloric acid (1.0 M, 50 μL). The reaction mixture was stirred at RT for 16 h and then concentrated in vacuo employing toluene (3 × 2.5 mL) to remove water azeotropically. The residue was dissolved in anhydrous dichloromethane (1.0 mL); pyridine (15 μL, 0.19 mmol), DMAP (cat.), and acetic anhydride (34 μL, 0.36 mmol) were added, and the reaction mixture was stirred at RT for 1.5 h. The solution was cooled to 0 °C, and the reaction was quenched by the dropwise addition of saturated aqueous $NaHCO_3$ solution (1.0 mL). The mixture was partitioned between water (5 mL) and ether (5 mL); the aqueous layer was separated and extracted with ether (3 × 5 mL). The combined organic fractions were washed with brine (15 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The residue was purified by flash column chromatography (silica gel, 1:1 petrol/ether) to furnish the *title compound* (**51**) as a colorless oil (7.7 mg, 95%). R_f 0.28 (1:1 petrol/ether). ν_{max}/cm^{-1} (thin film): 3065w, 3031w, 2959m, 2930m, 2873m, 1743s, 1497w, 1454w, 1371m, 1229s, 1072m, 1038m, 906w, 768w, 738w, 698m, 672w. δ_H (400 MHz, $CDCl_3$): 1.31 (1H, ddd, *J* 14.4, 12.8, 2.0) and 2.00 (1H, dt, *J* 14.4, 3.8, CH$_2$), 2.06 and 2.10 (2 × 3H, 2 × s, 2 × OAc), 2.40−2.50 (1H, m, C*H*CH$_2$-OAc), 3.32 (1H, dd, *J* 10.0, 2.6, C*H*(OBn)CHOAc), 3.76 (1H, dd, *J* 11.2, 10.0, CHCl), 3.93−3.96 (1H, m, C*H*(OBn)CH$_2$), 4.20 (1H, dd, *J* 11.2, 2.2) and 4.31 (1H, dd, *J* 11.2, 4.4, CH_2OAc), 4.50 and 4.61 (2 × 1H, 2 × d, *J* 12.4, CH_2Ph), 4.64 and 4.77 (2 × 1H, 2 × d, *J* 12.0, CH_2Ph), 5.63 (1H, t, *J* 10.0, C*H*OAc), 7.28−7.38 (10H, m, 2 × Ph). δ_C (100.6 MHz, $CDCl_3$): 20.6, 20.8, 30.4, 37.5, 60.6, 64.5, 71.8, 72.0, 72.1, 74.6, 80.9, 127.3, 127.5, 127.6, 128.2, 128.3 (two peaks), 137.9, 138.3, 169.6, 170.6. *m/z* (ES$^+$): 483 (MNa$^+$, ^{35}Cl, 67%), 478 (MNH_4^+, ^{35}Cl, 100), 454 (17), 279 (15), 153 (13). Accurate mass (ES$^+$): found, 478.1994; $C_{25}H_{33}NO_6Cl$ (MNH_4^+, ^{35}Cl) requires 478.1996.

(1*S,4*S**,7*R**,4′*S**,5′*S**)- and (1R*,4*R**,7*R**,4′*S**,5′*S**)-7-[5-(*tert*-Butyl)-2,2-dimethyl-1,3-dioxolan-4-yl]-2,3-dioxabicyclo[2.2.2]-oct-5-ene (53) and (54).** A stirred solution of dioxolane **45** (261 mg, 1.11 mol) and methylene blue indicator (20 μL, 0.05% w/v in dichloromethane) in anhydrous dichloromethane (165 mL) was cooled to −78 °C. The resulting mixture was irradiated with a tungsten filament lamp (300 W) while oxygen was passed through the solution; after 4.5 h the solution was warmed to RT and filtered through a short plug of silica gel and Celite; the residue was washed with dichloromethane (3 × 20 mL), and the filtrate was concentrated in vacuo. The resulting material was purified by flash column chromatography (silica gel, 5:1 petrol/ether) to furnish a mixture of the diastereomeric *endoperoxides* **53** and **54** as a colorless crystalline solid (225 mg, 53:54 = 2:1, 76%). Data for **53** (which could be partially separated from **54**) are as follows. R_f 0.44 (1:1 petrol/ether). ν_{max}/cm^{-1} (KBr disk): 2961s, 2871m, 1480w, 1469w, 1441w, 1396w, 1380m, 1370s, 1335w, 1301w, 1247s, 1216s, 1175w, 1157m, 1094w, 1073m, 1053m, 1028m, 996w, 960w, 948w, 881w, 867w, 756s, 711w, 667m. δ_H (400 MHz, $CDCl_3$): 0.89 (9H, s, *t*-Bu), 1.18 (1H, ddd, *J* 13.2, 4.8, 1.6, C*H*H′), 1.41 and 1.47 (2 × 3H, 2 × s, CMe$_2$), 2.35 (1H, ddd, *J* 13.2, 9.2, 4.4, CH*H*′), 2.75 (1H, tdd, *J* 9.2, 4.8, 3.2, CH-(OCMe$_2$)C*H*), 3.40 (1H, dd, *J* 9.2, 4.8, C*H*(OCMe$_2$)CH), 3.67

(1H, d, J 4.8, t-BuCH), 4.64−4.68 and 4.87−4.91 (2 × 1H, 2 × m, CHO−OCH), 6.68−6.71 (2H, m, CH=CH). δ_C (100.6 MHz, $CDCl_3$): 26.1, 27.0, 27.5, 28.6, 33.4, 38.8, 70.2, 72.2, 80.1, 88.8, 109.6, 131.3, 132.4. m/z (CI^+): 286 (MNH_4^+, 7%), 269 (MH^+, 45), 253 (64), 211 (100), 194 (37), 185 (90), 177 (51), 169 (33), 157 (33).. Accurate mass (CI^+): found, 286.2014; $C_{15}H_{28}NO_4$ (MNH_4^+) requires 286.2018. Data for **54** (obtained in admixture with **53**) are as follows. R_f 0.42 (1:1 petrol/ether). ν_{max}/cm^{-1} (KBr disk): 3066w, 3017m, 2983m, 2960s, 2871m, 1480w, 1468w, 1458w, 1441w, 1396w, 1380m, 1370s, 1335w, 1301w, 1247s, 1216s, 1179w, 1157m, 1087m, 1068m, 1053m, 1027m, 994w, 960w, 926w, 908w, 867w, 757s, 711w, 668m. δ_H (400 MHz, $CDCl_3$): 0.99 (9H, s, t-Bu), 1.39 and 1.47 (2 × 3H, 2 × s, CMe_2), 1.60 (1H, ddd, J 13.2, 10.8, 2.0) and 1.80 (1H, ddd, J 13.2, 4.8, 4.0, CH_2), 1.91 (1H, tdd, J 10.8, 4.8, 1.6, CH-($OCMe_2$)CH), 3.68 (1H, d, J 3.4, t-BuCH), 4.28 (1H, dd, J 10.8, 3.4, CH($OCMe_2$)CH), 4.61−4.66 and 4.89−4.93 (2 × 1H, 2 × m, CHO−OCH), 6.66−6.69 (1H, m) and 6.77 (1H, ddd, J 8.4, 6.4, 2.0, CH=CH). δ_C (100.6 MHz, $CDCl_3$): 25.2, 26.3, 27.9, 29.3, 34.0, 39.2, 70.3, 71.6, 78.7, 89.7, 109.8, 132.4, 132.8. m/z (CI^+): 269 (MH^+, 46%), 253 (20), 211 (25), 195 (20), 185 (100), 175 (21).. Accurate mass (CI^+): found, 269.1756; $C_{15}H_{25}O_4$ (MH^+) requires 269.1753.

(4*S,5*S**,1′*S**,2′*S**,5′*S**)-5-(*tert*-Butyl)-4-(2,5-dibenzyloxycyclohexa-3-enyl)-2,2-dimethyl-1,3-dioxolane (56).** To a stirred solution of endoperoxide **53** (20 mg, 0.075 mol) in anhydrous tetrahydrofuran (1.5 mL) cooled to 0 °C was added $LiAlH_4$ (7.2 mg, 0.19 mmol), and the reaction mixture was stirred at 0 °C for 30 min and then at RT for 15 min. The reaction mixture was recooled to 0 °C, quenched by the dropwise addition of saturated aqueous potassium sodium tartrate solution (1.5 mL), and stirred for 15 min. The mixture was partitioned between water (15 mL) and ethyl acetate (15 mL); the aqueous phase was separated and extracted with ethyl acetate (3 × 15 mL). The combined organic fractions were washed with brine (25 mL), dried ($MgSO_4$), and the solvents were removed in vacuo to furnish the crude diol (**55**) as a pale yellow solid. After azeotropic removal of residual moisture with toluene (3 × 5 mL), the diol was dissolved in anhydrous DMF (3.0 mL), and the solution was cooled to 0 °C. Benzyl bromide (36 μL, 0.30 mmol) was added, followed by NaH (12 mg of a 60% dispersion in mineral oil, 0.30 mmol), and the reaction mixture was warmed slowly to RT over 16 h. The solution was cooled to 0 °C, and the reaction was quenched by the dropwise addition of methanol (500 μL); the resulting mixture was partitioned between water (25 mL) and ether (15 mL). The aqueous phase was separated and extracted with ether (3 × 15 mL); the combined organic fractions were washed with brine (25 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The residual oil was azeotroped with toluene (2 × 10 mL) to remove traces of DMF. Purification by flash column chromatography (silica gel, 5:1 petrol/ether) gave the *title compound* (**56**) as a colorless oil (27.2 mg, 81%). R_f 0.40 (5:1 petrol/ether). ν_{max}/cm^{-1} (thin film): 3030w, 2952m, 2869m, 1497w, 1480w, 1454w, 1377w, 1367m, 1240m, 1216w, 1170w, 1065s, 1028m, 914w, 733m, 697s. δ_H (400 MHz, $CDCl_3$): 0.91 (9H, s, t-Bu), 1.37 and 1.40 (2 × 3H, 2 × s, CMe_2), 1.82 (1H, ddd, J 14.0, 11.6, 4.0) and 1.95 (1H, ddt, J 14.0, 3.6, 1.0, CH_2), 2.37 (1H, dddd, J 11.6, 8.0, 3.6, 2.0, CH($OCMe_2$)CH), 3.71 (1H, dd, J 8.8, 2.0, CH($OCMe_2$)CH), 3.96 (1H, td, J 4.0, 3.6, CH_2CHOBn), 4.13 (1H, d, J 8.8, t-BuCH), 4.35 (1H, ddt, J 8.0, 2.6, 1.0, CH(OBn)CH=), 4.54 and 4.70 (2 × 1H, 2 × d, J 11.4, CH_2Ph), 4.60 (2H, s, CH_2Ph), 5.98 (1H, ddt, J 10.2, 4.0, 1.0) and 6.06 (1H, dd, J 10.2, 2.6, CH=CH), 7.26−7.40 (10H, m, 2 × Ph). δ_C (100.6 MHz, $CDCl_3$): 26.3, 27.4, 27.8, 32.2, 32.5, 36.2, 69.6, 70.4, 70.7, 73.5, 80.5, 84.8, 107.1, 127.5, 127.6, 127.7, 127.8, 128.2, 128.3, 128.4, 131.4, 138.5, 140.0. m/z (ES^+): 473 (MNa^+, 100%), 468 (MNH_4^+, 57), 451 (MH^+, 12), 343 (98), 285 (23). Accurate mass (ES^+): found, 473.2668; $C_{29}H_{38}O_4Na$ (MNa^+) requires 473.2668.

(4*S,5*S**,1′*S**,2′*R**,3′*S**,4′*R**,5′*S**)-5-(*tert*-Butyl)-4-[2,3,4,5-tetra(benzyloxy)cyclohexyl]-2,2-dimethyl-1,3-dioxolane (58).** To a stirred solution of alkene **56** (24.1 mg, 0.053 mmol) in tetrahydrofuran (2.5 mL) was added NMO (7 mg, 0.06 mmol) and OsO_4 (cat.); the reaction mixture was stirred at RT for 1 h. The reaction was quenched by the addition of dilute aqueous Na_2SO_3 solution (10% w/v, 2.5 mL), and the mixture was partitioned between water (10 mL) and ethyl acetate (10 mL); the aqueous phase was separated and extracted with ethyl acetate (3 × 10 mL). The combined organic fractions were washed with brine (25 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The residue (crude diol **57**) was azeotroped with toluene (3 × 5 mL) and then dissolved in anhydrous DMF (2.5 mL), and the solution was cooled to 0 °C. Benzyl bromide (26 μL, 0.22 mmol) was added, followed by NaH (9 mg, 0.23 mmol). The reaction mixture was allowed to warm to RT over 12 h. The solution was cooled to 0 °C, and the reaction was quenched by the dropwise addition of methanol (500 μL); the resulting mixture was partitioned between water (10 mL) and ether (10 mL). The aqueous phase was separated and extracted with ether (3 × 10 mL); the combined organic fractions were washed with brine (25 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The residual oil was azeotroped with toluene (2 × 10 mL) to remove traces of DMF. Purification by flash column chromatography (silica gel, 7:1 petrol/ether) gave *benzylated tetraol* **58** as a colorless oil (27.4 mg, 77%). R_f 0.30 (7:1 petrol/ether). ν_{max}/cm^{-1} (thin film): 3056w, 3030w, 2978w, 2952m, 2932m, 2869m, 1496w, 1453m, 1367m, 1247w, 1208w, 1072s, 1027m, 734m, 697s. δ_H (400 MHz, $CDCl_3$): 0.89 (9H, s, t-Bu), 1.39 and 1.47 (2 × 3H, 2 × s, CMe_2), 1.74 (1H, dt, J 14.2, 4.0) and 2.04 (1H, ddd, J 14.2, 11.2, 4.0, CH_2), 2.20−2.30 (1H, m, CH($OCMe_2$)CH), 3.73 (1H, td, J 4.0, 3.6, CH_2CHOBn), 3.81 (1H, dd, J 4.0, 3.6, CH(OBn)CHOBn), 3.84−3.87 (1H, m, CH($OCMe_2$)CH), 3.89 (1H, dd, J 8.2, 3.6, CH(OBn)CHOBn), 4.09 (1H, d, J 7.2, t-BuCH), 4.18 (1H, t, J 8.2, CH(OBn)CH), 4.43 and 4.49 (2 × 1H, 2 × d, J 11.6, CH_2Ph), 4.57 and 4.66 (2 × 1H, 2 × d, J 11.6, CH_2Ph), 4.64 and 4.72 (2 × 1H, 2 × d, J 12.2, CH_2Ph), 4.70 (2H, s, CH_2Ph), 7.23−7.38 (20H, m, 4 × Ph). δ_C (100.6 MHz, $CDCl_3$): 26.4, 27.4, 28.5, 30.8, 32.8, 33.2, 71.2, 72.5, 72.6, 72.7, 74.9, 76.5, 77.0, 80.0, 82.1, 86.9, 107.8, 127.3−128.3 (overlapping), 138.7, 138.8, 138.9, 139.0. m/z (ES^+): 687 (MNa^+, 45%), 682 (MNH_4^+, 30), 665 (MH^+, 100), 515 (12), 454 (14), 413 (12), 391 (18), 342 (19), 301 (15), 279 (19), 226 (20). Accurate mass (ES^+): found, 665.3836; $C_{43}H_{53}O_6$ (MH^+) requires 665.3842.

(1*S,2*S**,1′*R**,2′*R**,3′*S**,4′*R**,5′*S**)-1-[2,3,4,5-Tetra(benzyloxy)cyclohexyl]-3,3-dimethylbutan-1,2-diol (59).** To a stirred solution of dioxolane **58** (23.3 mg, 0.035 mmol) in tetrahydrofuran (2.0 mL) and water (1.0 mL) was added TFA (2.0 mL), and the mixture was stirred at RT for 1.5 h. The solution was concentrated in vacuo employing toluene (3 × 10 mL) to remove water azeotropically. The residue was purified by flash column chromatography (silica gel, 5:1 petrol/ether) to furnish *diol* **59** as a colorless oil (20.3 mg, 93%). R_f 0.35 (2:1 petrol/ether). ν_{max}/cm^{-1} (thin film): 3435m, 3064w, 3030w, 2949m, 2927m, 2865w, 1496w, 1454m, 1390w, 1363w, 1309w, 1207w, 1097s, 1066s, 1028m, 734s, 697s. δ_H (400 MHz, $CDCl_3$): 0.91 (9H, s, t-Bu), 1.52 (1H, ddd, J 14.2, 12.0, 2.8) and 1.92 (1H, ddd, J 14.2, 4.0, 3.6, CH_2), 2.09 (1H, dddd, J 12.0, 9.2, 7.6 and 4.0, CH(OH)CH), 3.13 (1H, s, t-BuCH), 3.69 (1H, td, J 3.6, 2.8, CH(OBn)CH_2), 3.78 (1H, d, J 7.6, CH(OH)-CH), 3.83 (1H, dd, J 3.6, 2.8, CH(OBn)CHOBn), 3.93 (1H, dd, J 9.2, 2.8, CH(OBn)CH(OBn)), 4.00 (1H, t, J 9.2, CH(OBn)-CH), 4.34 and 4.54 (2 × 1H, 2 × d, J 12.0, CH_2Ph), 4.59 (2H, s, CH_2Ph), 4.61 and 4.73 (2 × 1H, 2 × d, J 12.0, CH_2Ph), 4.71 and 5.08 (2 × 1H, 2 × d, J 10.8, CH_2Ph), 7.23−7.36 (20H, m, 4 × Ph). δ_C (125.7 MHz, $CDCl_3$): 26.3, 26.8, 34.9, 39.7, 70.8, 72.5, 72.9, 73.0, 74.0, 74.1, 76.1, 77.1, 81.1, 81.7, 127.4−128.3 (overlapping), 137.7, 138.2, 138.3, 138.5. m/z (ES^+): 647 (MNa^+, 66%), 625 (MH^+, 100). Accurate mass (ES^+): found, 625.3526; $C_{40}H_{49}O_6$ (MH^+) requires 625.3529.

(1*S,2*R**,3*S**,4*R**,5*R**)-1,2,3,4-Tetra(benzyloxy)-5-(hydroxymethyl)cyclohexane (60).** To a stirred suspension of

$NaIO_4$ on silica gel (25 wt %, 86 mg, 0.10 mmol) in tetrahydrofuran (1.0 mL) was added a solution of diol **59** (11.6 mg, 0.019 mmol) in tetrahydrofuran (1.0 mL). The reaction mixture was stirred vigorously at RT for 3 h and then filtered through Celite and washed with tetrahydrofuran (2 × 2 mL). The filtrate was added dropwise to a stirred solution of $NaBH_4$ (4 mg, 0.11 mmol) in tetrahydrofuran (1.0 mL) and methanol (500 μL) and stirred at RT for 25 min. The reaction was quenched by the addition of saturated aqueous NH_4Cl solution (5 mL); the aqueous phase was extracted with ether (3 × 5 mL), and the combined organic fractions were washed with brine (15 mL), dried ($MgSO_4$), and the solvents were removed in vacuo. The residual oil was purified by flash column chromatography (silica gel, 1:1 petrol/ether) to furnish the *title compound* (**60**) as a colorless oil (7.7 mg, 77%). R_f 0.57 (ether). ν_{max}/cm^{-1} (thin film): 3469m, 3090w, 3063w, 3030m, 2923m, 2861m, 1953w, 1877w, 1813w, 1724w, 1605w, 1513w, 1496m, 1453m, 1391w, 1362w, 1323w, 1306w, 1251w, 1234w, 1207w, 1154w, 1091s, 1073s, 1028m, 911w, 734s, 697s. δ_H (500 MHz, $CDCl_3$): 1.64 (1H, ddd, *J* 14.0, 12.5, 3.0) and 1.73 (1H, dt, *J* 14.0, 3.5, CH_2), 2.00−2.10 (1H, m, C*H*CH_2OH), 2.23 (1H, br s, CH_2O*H*), 3.60−3.65 (2H, m, C*H*$_2$OH), 3.68 (1H, dt, *J* 3.5, 3.0, CH_2C*H*OBn), 3.80 (1H, t, *J* 3.0, CH_2CH(OBn)C*H*), 3.84 (1H, t, *J* 9.5, C*H*(OBn)CHCH_2OH), 3.89 (1H, dd, *J* 9.5, 3.0, C*H*(OBn)CH-(OBn)CH), 4.32 and 4.48 (2 × 1H, 2 × d, *J* 12.0, C*H*$_2$Ph), 4.59 and 4.76 (2 × 1H, 2 × d, *J* 12.0, C*H*$_2$Ph), 4.60 and 4.67 (2 × 1H, 2 × d, *J* 11.0, C*H*$_2$Ph), 4.69 and 5.03 (2 × 1H, 2 × d, *J* 11.0, C*H*$_2$Ph), 7.26−7.39 (20H, m, 4 × Ph). δ_C (125.7 MHz, $CDCl_3$): 26.8, 39.0, 65.9, 70.7, 72.5, 72.9, 74.6, 74.9, 76.0, 80.5, 82.2, 127.2−128.4 (overlapping), 138.3, 138.4, 138.6 (two peaks). *m/z* (ES$^+$): 561 (MNa$^+$, 100%), 539 (MH$^+$, 69), 454 (26), 391 (33), 342 (18), 326 (22). Accurate mass (ES$^+$): found, 539.2792; $C_{35}H_{39}O_5$ (MH$^+$) requires 539.2797.

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Supporting Information Available: Copies of ^{13}C NMR spectra for new compounds, 2D NMR spectra for **51**, and crystallographic data for **40**. This material is available free of charge via the Internet at http://pubs.acs.org.

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